THE TRANSITION METAL-ALKENE BOND AND FIVE-COORDINATION IN IRIDIUM(I) COMPLEXES

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aan mijn ouders,

aan Ria, Danny en Pieter

C O N T E N T S

CHAPTER 1

INTRODUCTION

Transition metal complexes often act as homogeneous catalysts in a variety of reactions involving alkenes. This rapidly expanding field of research, which has been reviewed by several authors (1-4), comprises hydrogenation, oxidation, isomerisation, hydroformylation as well as oligo- and polimerisation reactions. During these processes transition metal-alkene complexes are formed as reactive intermediates. The role of the metal centre in catalysts is twofold. First, it increases the probability of reaction between two reactants by bringing them together on two adjacent coordination sites. The availability of a vacant side at the metal suitable for substrate coordination is therefore generally considered to be a prerequisite for catalytic activity. Among the square planar transition metal complexes with a d^8 electron configuration many homogeneous catalysts are found. Their ability to expand their coordination sphere to five ligands gives them a coordinative unsaturated character. In catalytic systems the resulting five-coordinated species may function either as a labile intermediate in a ligand substitution reaction or as a reactive intermediate in which the alkene is able to react with one of the other ligands. The second role of the metal centre is to change the reactivity of the reactants on coordination. So, alkenes may become susceptible to nucleophilic attack in palladium(II) or platinum(II) complexes (1,5,6) and the course of electrophilic addition reactions may be changed by coordination, providing for example a useful synthetic path to substituted cyclo-octatetraene derivatives which are otherwise difficult to attain (7).

The transition metal-alkene bond is generally described by the Dewar, Chatt, Duncanson model (8,9). This model involves a bond of σ-symmetry formed by donation of alkenic electrons to an empty metal hybrid orbital which is complemented by a bond of

π-symmetry in which electron density from a filled metal hybrid orbital is backdonated to an empty antibonding orbital of the alkene. It is often difficult to gain a detailed insight into the extent to which the components of the metal-alkene bond contribute to the various properties of this bond. Qualitatively it may be expected that both components cooperate in their contribution to properties such as the transition metal-alkene bond strength or the weakening with the concomitant lengthening of the C = C bond on coordination.

Opposing contributions are expected in the partition of electron density between metal and alkene ligand. The barrier to rotation of the alkene around the metal-alkene bond is thought to be determined mainly by the π-component which is broken during this process. It must, however, be realised that increased σ-bonding may result in more steric hindrance with the adjacent ligands and thus in a higher barrier through shortening of the metal-alkene bond. The influence on the barrier exerted by the π-accepting properties of the other ligands is demonstrated in this thesis. The influence of electron withdrawing substituents on the stability of transition metal-alkene complexes suggests that in silver(I) and copper(I) complexes the σ-bond is more important, whereas in group VIII metal complexes under which many homogeneous catalysts are found, the π-back bond seems to contribute more to the stability than does the σ-component. In tetrafluoroethylene complexes of these metals, π-backbonding is favoured by the presence of the electronegative fluorine substituents. This is illustrated by the absence of C_2F_4 rotation around the metal-C_2F_4 bond and the enhanced coordination properties of the metal towards Lewis bases. Although these complexes are more stable than the corresponding ethylene complexes, the displacement of ethylene by tetrafluoroethylene at rhodium(I) is slower by a factor of 10^6 than ethylene exchange (10). From this behaviour it was concluded that the development of the

σ-component of the transition metal-alkene bond governs the formation of the transition state in these alkene substitution reactions. This view is, however, not supported by our investigations.

In this thesis several of the above-mentioned aspects of the transition metal-alkene bond and the stability of five-coordinated complexes are discussed in connection with the synthesis of new iridium(I) compounds. The chemistry of iridium(I), which is a member of the third transition row, distinguishes itself from the chemistry of the corresponding second-row member, rhodium(I), by the more facile conversion to the oxidation state III and the higher ability to form five-coordinated complexes. The former may be ascribed to the lower oxidation potential of iridium(I) and the latter to the better overlap of its orbitals with the ligand orbitals. Both properties are expected to favour the π-backbonding capacity of iridium(I).

The isolation of iridium(I) complexes is often obstructed by their sensitivity towards oxidation, unless the metal is protected by coordination by a π-accepting ligand such as carbonmonoxide or a chelating alkene. These ligands are however difficult to substitute. In Chapter 2 the detailed synthesis under non-oxidizing conditions is given of chlorobis(cyclooctene) rhodium(I) and iridium(I) with the formula $[MCl(C_8H_{14})_2]_n$, in which the ligands lend themselves easier to substitution.

Chapter 3 describes the replacement of the cyclooctene ligands in chloro- and bromo- bis(cyclooctene)iridium(I) by other alkenes among which monoenes, acyclic conjugated dienes and cyclic polyenes. The resulting complexes are compared with the corresponding rhodium(I) species known from the literature.

Chapter 4 reports on the reorientations of the ethylene ligands in solid $IrCl(C_2H_4)_4$ on the basis of the magnetic relaxation behaviour of this complex as a function of temperature.

In Chapter 5 the reactions of C_2F_4 with $[IrCl(C_2H_4)_2]_2$ and $Ir(acac)(C_2H_4)_2$ and the reactions of Lewis bases with the re-

sulting C_2F_4-complexes are described. Ethylene exchange and the barrier to rotation of ethylene are discussed on the basis of PMR experiments with $Ir(acac)(C_2H_4)_2$ and $Ir(acac)(C_2H_4)(C_2F_4)$.

Chapter 6 describes the formation of four- and five-coordinated addition products of chlorobis(triphenylphosphine)iridium(I). The stability of five-coordinated complexes of the type $IrCl(PPh_3)_2XY$ is discussed on the basis of the donor and acceptor properties of the ligands X and Y.

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CHAPTER 2

THE SYNTHESIS OF CHLOROBIS(CYCLOOCTENE)RHODIUM(I) AND -IRIDIUM(I)*)

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The cyclooctene compounds $[MCl(C_8H_{14})_2]_n$, with M = Rh or Ir, are important starting materials for the preparation of rhodium(I) and iridium(I) complexes(1,2). The compound $[RhCl(C_8H_{14})_2]_n$ can be separated in varying yields (35-60%) from solutions of rhodium(III) trichloride trihydrate and cyclooctene in ethanol (3) after standing 3-5 days. Di[μ-chlorobis(cyclooctene)iridium] can be prepared in 40% yield by refluxing chloroiridic(IV) acid and cyclooctene in 2-propanol (4). The resulting product is always contaminated with an iridium hydride complex. The following modifications give better yields (70-80%) and an iridium(I) complex of higher purity.

A. CHLOROBIS(CYCLOOCTENE)RHODIUM(I)

$$RhCl_3 + 2C_8H_{14} + CH_3CH(OH)CH_3 \longrightarrow RhCl(C_8H_{14})_2 + CH_3COCH_3 + 2HCl$$

Procedure

In a 100-ml., three-necked, round-bottomed flask, 2 g. (7.7 mmoles) of rhodium trichloride trihydrate is dissolved in an oxygen-free mixture of 40 ml. of 2-propanol and 10 ml. of water. Cyclooctene (6 ml.) is added. The solution is stirred for about 15 minutes under nitrogen. The flask is then closed and allowed to stand at room temperature for 5 days. The resulting reddish-brown crystals are collected on a filter, -ashed with ethanol, dried under vacuum, and stored under nitrogen at -5°C. The yield is

*Inorg. Synth. 14, 94 (1973).

2.0 g (74%). Anal. Calcd. for $RhC_{16}H_{28}Cl$: Rh, 28.72; C, 53.56; H, 7.81; Cl, 9.91. Found: Rh, 28.55; C, 53.76; H, 7.89; Cl, 9.76.

Properties

The solubility of $[RhCl(C_8H_{14})_2]_n$ in benzene and chloroform is too low for molecular-weight measurements. Its reddish-brown color darkens slowly in air.

B. DI[μ-CHLOROBIS(CYCLOOCTENE)IRIDIUM(I)]

$$2(NH_4)_3IrCl_6 + 4C_8H_{14} + 2CH_3CH(OH)CH_3 \longrightarrow [IrCl(C_8H_{14})_2]_2 + 6NH_4Cl + 2CH_3COCH_3 + 4HCl$$

Procedure

In a 250-ml, three-necked, round-bottomed flask, fitted with a nitrogen inlet and a reflux condenser, 6 g (0.01 mole) of ammonium hexachloroiridate(III)*) (43.1% Ir) is suspended in an oxygen-free mixture of 30 ml of 2-propanol and 90 ml of water†. Cyclooctene (12 ml) is added. The mixture is refluxed on a water bath under a slow stream of nitrogen and with vigorous stirring for 3-4 hours. After cooling, the alcohol-water mixture is decanted, the last few milliliters being pipettet off. The orange oil remaining in the flask is allowed to crystallize under ethanol at 0°C. The yellow crystals are collected on a filter, washed with cold ethanol, dried under vacuum, and stored under nitrogen at room temperature. The yield is 4.7 g (80%). Anal. Calcd. for $Ir_2C_{32}H_{56}Cl_2$: C, 42.89; H, 6.25; Cl, 7.93. Found: C, 43.12; H, 5.97; Cl, 7.84.

*) Available from Johnson, Matthey Company Ltd., London, England

† Similar results are obtained by using sodium or potassium chloroiridite(III)

Properties

The results of molecular-weight measurements on a freshly prepared solution in benzene suggest a dimeric structure (found: M = 886; calcd., M = 895). In the solid state, $[IrCl(C_8H_{14})_2]_2$ decomposes slowly under the influence of atmospheric moisture. The compound is moderately soluble in benzene, chloroform, and carbon tetrachloride, but in general, these solutions are unstable for long periods of time. In comparison with the corresponding rhodium complex, this compound is more reactive in oxidative addition reactions. This is demonstrated by the formation of iridium hydrides during reaction with hydrogen or hydrogen chloride.

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CHAPTER 3

CHLORO- AND BROMO-(ALKENE)IRIDIUM(I) COMPLEXES*)

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Summary

Chloro- and bromo-(alkene)iridium(I) complexes were prepared by the reaction of monoenes, acyclic conjugated dienes and cyclic polyenes with the cyclooctene complexes $[IrX(C_8H_{14})_2]_n$ with X = Cl or Br.

$IrCl(C_2H_4)_4$ is an unstable penta-coordinated compound from which the planar chlorine-bridged dimer $[IrCl(C_2H_4)_2]_2$ is formed upon ethylene dissociation. From the absence of broadening of the ethylene PMR resonances in chloroform upon cooling to -60°C, low barriers to rotation of the ethylene ligands around the metal-alkene bond were concluded. In toluene the appearance at -60°C of the "frozen out"-situation for the equatorial ligands suggested a considerably higher barrier for these ligands in this solvent. The equatorial ethylene ligands show slow exchange with free ethylene by an associative mechanism. No exchange with the axial ethylene ligand could be detected.

Acyclic conjugated dienes formed penta-coordinated complexes of the type $IrX(alk)_2$.

1,5-Cyclooctadiene formed the dimer complexes $[IrX(C_8H_{12})]_2$ and the monomer complexes $IrX(C_8H_{12})_2$.

The investigation of the bromo compounds was limited to their identification by elementary analysis and by their IR spectrum in the 4000-400 cm^{-1} region. Their far-IR spectra were used as an aid in the assignment of the ν(Ir-Cl) in the corresponding chloro compounds.

*) Published as such in Inorganica Chimica Acta 6, 420 (1972)

From the comparison of the far-IR spectra of corresponding chloro(alkene)-rhodium(I) and -iridium(I) complexes it was concluded that the metal-alkene as well as the metal-chlorine bonds are stronger in the iridium(I) compounds.

Introduction (I)

In contrast to rhodium(I), relatively few alkene complexes of iridium(I) without strongly π-accepting ligands such as carbon monoxide or chelating alkenes are known. This is mainly due to the ease with which iridium(I), being a member of the third transition metal series, is oxidized to the oxidation state III. By consequence most of the iridium(I) complexes tend to be oxidized during the synthesis by oxidative addition reactions (2,3) or, alternatively, are protected from oxidation by the addition of a π-accepting ligand as carbon monoxide (4) or a chelating alkene (5).

The improved synthesis under non-oxidizing conditions of the halogenobis(cyclooctene)iridium(I) complexes, $[IrX(C_8H_{14})_2]_n$ with X = Cl or Br, of which the chloro complex was first reported by Shaw and Singleton (6), gave us the opportunity to prepare new iridium(I) complexes by replacing the cyclooctene ligands by other alkenes or by phosphine and arsine ligands (7). Analogous methods were reported (8-10) to prepare rhodium(I) complexes from the corresponding chlorobis(cyclooctene)rhodium(I), $RhCl(C_8H_{14})_2$. In this paper the reactions with alkenes and the properties of the resulting complexes will be discussed.

Experimental Section

Materials. $(NH_4)_3IrCl_6$ and K_2IrBr_6 were purchased from Messrs. Drijfhout, Amsterdam; cyclooctene, 1,5-cyclooctadiene,

isoprene and 1,3-trans-pentadiene from Fluka; and ethylene, propylene and butadiene from Air Liquide. All solvents were reagent-grade quality and degassed before use. All experiments were carried out under nitrogen or argon. The following complexes were prepared by literature methods: $[RhCl(C_2H_4)_2]_2$ (Ref. 21), $[RhCl(C_3H_6)_2]_2$ (Ref. 21), $RhCl(C_8H_{14})_2$ (Ref. 25), $RhCl(C_4H_6)_2$ (Ref. 25), $[RhCl(C_8H_8)]_2$ (Ref. 9) and $[IrCl(C_8H_{12})]_2$ (Ref. 5). The preparation and the analytical data of the other complexes prepared are given in Table I.

Measurements. IR-spectra were measured on Hitachi EPI-G 2 (4000-400 cm^{-1}) and Hitachi EPI-L (700-200 cm^{-1}) spectrometers. PMR spec-ra were recorded on the Varian spectrometers A-60 and HA-100, equipped with a variable temperature probe. X-ray powder photographs were taken with a Debye-Scherrer camera, using Cu-Kα radiation. Microanalyses were carried out by Dr A. Bernhardt, Mikroanalytisches Laboratorium, Elbach über Engelskirchen, Germany and TNO, Utrecht, Holland. Molecular weight measurements were carried out with a Hitachi-Perkin Elmer osmometer.

Results and Discussion

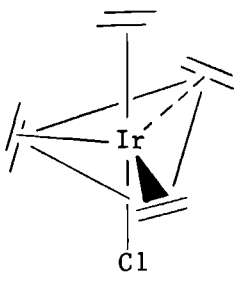
(a) Monoene complexes

Bis[μ-chlorobis(cyclooctene)iridium(I)], $[IrCl(C_8H_{14})_2]_2$ (1a)*) was prepared in high yield by refluxing ammonium chloroiridite, $(NH_4)_3IrCl_6.H_2O$, with cyclooctene in a 2-propanol/water mixture. The preparation of the corresponding bromo compound, $[IrBr(C_8H_{14})_2]_n$ (1b) proceeds analogously from K_2IrBr_6. The compounds are stable under vacuum and under nitrogen, but decompose slowly in air under the influence of moisture. In solutions 1a is unstable, especially in halogen-containing solvents in which it is probably oxidized, as may be concluded from the isolation of a precipitate from old tetrachloride solutions, which gives a good analysis for $IrCl_3(C_8H_{14})$. Molecular weight

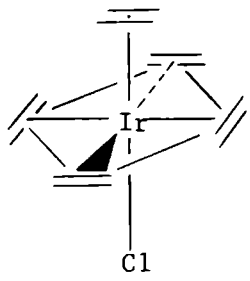
*) Underlined numbers refer to the compounds in Table I

measurements on the relatively stable benzene solution showed that 1a was present in solution as a dimeric species. The far-IR spectrum shows absorptions at 318(ms), 302(m) and 273(s) (Table II) which are assigned to iridium-chlorine stretching vibrations, ν(Ir-Cl), because of the absence of absorption bands in this region of the spectrum of (1b).

Chlorotetrakis(ethylene)iridium(I), $IrCl(C_2H_4)_4$ (2), is prepared by treating a suspension of 1a in heptane with ethylene at 0^oC and subsequently cooling to -50^oC. Up to 0^oC, it is stable under ethylene, but at room temperature it slowly decomposes under formation of butenes. Under nitrogen it is only stable below about -50^oC. At higher temperatures, it looses two molecules of ethylene and dimerizes to $[IrCl(C_2H_4)_2]_2$ (3). The bromo compound 1b does not react with ethylene. An X-ray investigation (11) showed 2 to be monomeric and to have a trigonal bipyramidal structure (I) with one axial and three equatorial in-plane ethylene ligands. The iridium atom is situated slightly out of the equatorial plane toward the axial ethylene ligand. The far-IR spectrum (CsI-pellet) shows three absorptions of medium intensity in the $\nu(Ir-C_2H_4)$ region at 505, 397 and 372 cm^{-1}. The ν(Ir-Cl) band at 280 cm^{-1} has a broad shoulder centered at 308 cm^{-1} (Table II). The PMR spectrum at -20^oC of a chloroform solution of 2 (Fig. 1a) shows two sharp resonances with an



(I)



(II)

Table I. Preparation and analysis of halogeno(alkene)iridium(I) complexes.

Compound	Starting from	Procedure	Yield (%)	Elem. analysis (calc./found) C	H	Cl	Br	Properties
1a $[IrCl(C_8H_{14})_2]_2$	2g$(NH_4)_2IrCl_6$ H_2O and 4 ml cyclooctene in 10 ml 2 propanol + 30 ml water	reflux for 2 h, cool, decant, cryst oil under ethanol at 0°C, wash 2x with ethanol, dry under vacuum over P_2O_5, store under argon	80	42.9 43.0	6.3 6.1	7.9 7.8		yellow crystals, mol wt 887 (40°C, benzene)(theor 896), m.p. 168°C (dec.)
1b $[IrBr(C_8H_{14})_2]_2$	1 g K_2IrBr_6 and 2 ml cyclooctene in 5 ml 2 propanol + 15 ml water	heat for 6 h at 55-60°C, etc. see *1a*	70	39.2 38.0	5.7 5.7		16.3 17.0	brown-yellow, dec. >120°C without melting
2 $IrCl(C_2H_4)_4$	0.5 g *1a* suspended in 5 ml heptane	bubble through C_2H_4 at 0°C until clear-red solution (suspension above sintered-glass filter with cooling device), cryst. by rapid cooling to −50°C, filter under C_2H_4 at −50°C, recryst. under C_2H_4 from heptane	65					white needles, stable under C_2H_4 <0°C, stable in vacuo <−50°C
3 $[IrCl(C_2H_4)_2]_2$	*2*	decomposition at room temperature under argon, store under nitrogen at −20°C		16.9 18.5	2.8 2.8	12.5 12.1		red, dec. >90°C without melting
4 $[IrCl(C_2H_4)_2]_2$	soln. of *3* in iso-pentane, sat. with C_2H_4	bubble through propylene at room temp., evaporate soln. to dark-red oil, store 2 days at −30°C until solidification	90	23.2 23.0	3.9 3.7	11.4 11.3		red oil
5a $IrCl(C_4H_6)_2$	fresh soln. of 0.1 g *1a* (or *3*) in 10 ml benzene	bubble through butadiene at room temp. immediate cryst., recryst. from CH_2Cl_2	75	28.6 28.6	3.6 3.7	10.6 10.3		white prisms; m.p. 178-181°C (dec.)
5b $IrBr(C_4H_6)_2$	as *5a* from *1b*	see *5a*, wash with ethanol and dry under vacuum	74	25.3 25.9	3.2 3.4		21.1 23.2	light-brown, m.p. 114-118°C (dec.)
6a $IrCl(isoprene)_2$	0.5 g *1a* (or *3*) suspended in 5 ml isoprene	immediate cryst., filter off, wash with hexane, dry under vacuum	74	33.0 33.1	4.4 4.6	9.8 9.8		off-white chystals, m.p. 91-95°C (dec.)
6b $IrBr(isoprene)_2$	as *6a* from *1b*	see *6a*	50	29.4 29.2	3.9 4.0		19.6 20.1	light-brown, dec. >140°C without melting
7a $IrCl(1,3\text{-tr. pentadiene})$	0.5 g *1a* (or *3*) suspended in 10 ml hexane + 2 ml 1,3-trans-pentadiene	after 5 min filter off precipitate, wash with hexane, dry under vacuum	82	33.0 33.2	4.4 4.6	9.8 9.9		off white, dec. >120°C without melting
8 $Rh_2Cl_2(C_4H_6)_4$	0.5 g $[RhCl(C_8H_{14})_2]_2$ suspended in 15 ml 100% ethanol	pass through at 40°C gaseous butadiene after few minutes cryst., filter off, dry in N_2 stream	78	32.8 32.8	4.1 4.2	16.2 16.0		yellow-greenish crystals, dec. 104-108°C
9b $[IrBr(C_5H_{10})]_2$	0.2 g *10b* in 25 ml hexane	filter off after 30 min., evaporate red filtrate to dryness	58	25.3 26.8	3.2 3.5		21.1 20.0	dark red, m.p. 196-199°C (dec.)
10a $IrCl(C_8H_{12})_2$	0.2 g *1a* suspended in 4 ml *pure* 1,5-cyclooctadiene	after 10 min filter off, wash 2x with pentane dry under vacuum	67	43.2 43.2	5.4 5.5	8.0 7.8		brown yellow, transition point 70°C (*10a*→yellow isomer of *9a*)
10b $IrBr(C_8H_{12})_2$	as *10a* from *1b*	see *10a*	60	39.4 40.7	4.9 5.3		16.4 15.8	brown, transition point 97°C, (*10b*→*9b*)
11 $[IrCl(C_8H_8)]_2$	0.5 g *1a* (or *3*) suspended in 5 ml *pure* cyclooctatetraene	after 20 min filter off, wash with alcohol, dry under vacuum	63	29.0 29.1	2.4 2.6	10.7 10.7		cream
12 $IrCl(C_4H_6)(C_5H_5N)$	0.18 g *11* suspended in 10 ml benzene	treat with 50.6 mg pyridine, after 5 h evaporate solvent with N_2, recryst. from alcohol	41	38.0 38.0	3.2 3.7	8.7 8.6		yellow crystals, elementary N calc. 3.4, found 3.5

Table II. Absorption frequencies (cm^{-1}) of halogene(alkene)-rhodium(I) and -iridium(I) complexes in the far-IR region

Compound	ν(M-X)	Other bands
$[RhCl(C_2H_4)_2]_2$	274(s), 260(sh), 248(s)	502(w), 407(sh), 398(s)
$[IrCl(C_2H_4)_2]_2$	292(sh), 289(m), 260(m)	537(w), 448(s), 308(vw)
$IrCl(C_2H_4)_4$	308(sh,br), 280(s)	505(m), 397(m), 372(w)
$[RhCl(C_3H_6)_2]_2$	290(m,br), 250(br)	508(m), 419(m), 386(s)
$[IrCl(C_3H_6)_2]_2$	290(s,br), 255(s,br)	537(s), 455(s,br), 440(vs,br), 405(w)
$[RhCl(C_8H_{14})_2]_2$	318(s), 290(m), 254(s)	548(s), 520(s), 414(m)
$[IrCl(C_8H_{14})_2]_2$	318(s), 302(m), 273(s), 270(sh)	578(s), 555(s), 545(s), 463(w), 436(s), 352(w)
$[IrBr(C_8H_{14})_2]_n$		577(m), 550(sh), 544(s), 434(m)
$[RhCl(C_8H_{12})]_2$	274(s), 254(s)	382(m), 247(sh)
$[RhBr(C_8H_{12})]_2$		379(m), 250(w), 244(w) Ref. 22
$[IrCl(C_8H_{12})]_2$	291(s), 258(m)	530(s), 508(m), 497(s), 428(vw), 413(s), 333(w), 327(sh)
$[IrCl(C_8H_{12})]_2$ (yellow isomer)	295(sh), 283(s), 265(m)	533(s), 512(m), 498(s), 417(s), 333(w)
$[IrBr(C_8H_{12})]_2$		529(m), 505(m), 495(m), 410(s), 330(w,br)
$IrCl(C_8H_{12})_2$	210(br)	585(m), 515(m), 477(w), 460(m), 426(w), 397(w), 376(w), 320(s), 271(s), 244(s)
$IrBr(C_8H_{12})_2$		584(m), 514(m), 475(m), 458(m), 425(w), 397(w), 375(w), 318(s), 270(s), 240(s)
$RhCl(C_4H_6)_2$	265(s), 261(sh)	504(m), 463(w), 443(s)
$IrCl(C_4H_6)_2$	288(vs), 283(sh)	528(m), 480(w), 463(s), 410(w), 323(m), 315(sh)
$IrBr(C_4H_6)_2$		520(m), 479(w), 459(s), 411(w), 323(s), 315(sh)
$IrCl(isoprene)_2$	278(s)	597(m), 540(m), 523(m), 475(m), 453(s), 334(sh), 327(br), 317(sh), 243(s), 222(m)
$IrBr(isoprene)_2$		597(m), 537(m), 521(s), 473(m), 452(s), 443(sh), 410(w), 356(w), 327(s), 310(s), 277(w), 245(s), 217(br)
$IrCl(1,3\text{-}tr\text{-pentadiene})_2$	290(s)	523(m), 505(m), 489(m), 443(s), 408(m), 317(m), 258(w), 254(w),, 210(m,br)

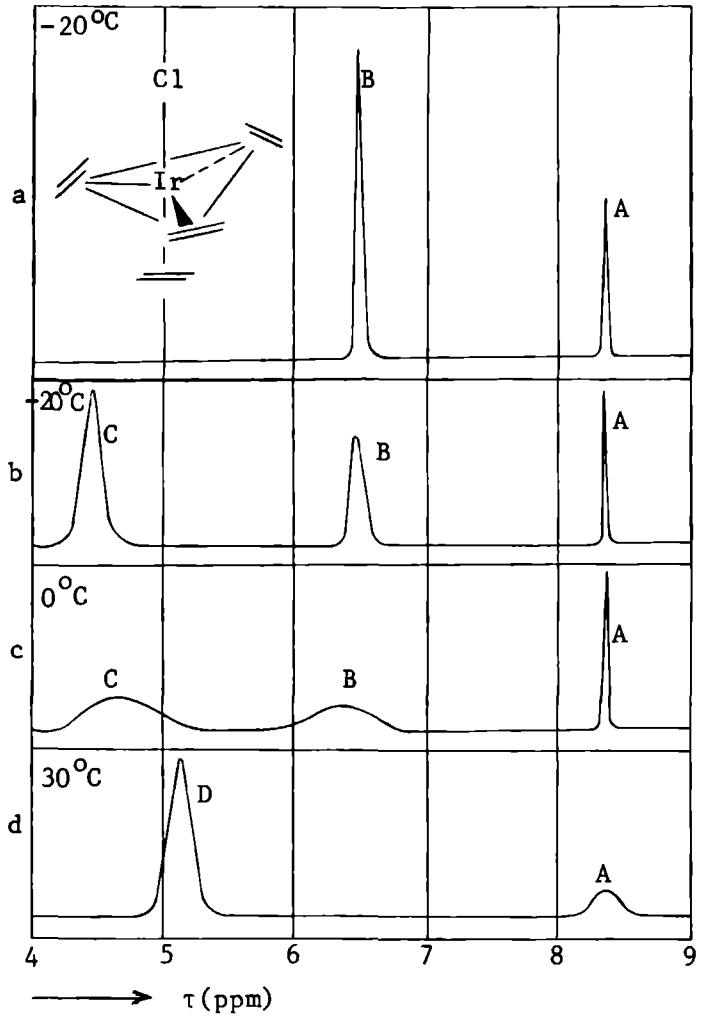


Fig. 1 Diagrammatic 100 MHz PMR spectra of solutions of $IrCl(C_2H_4)_4$ in chloroform at different temperatures: (a) complex as such, (b-d) complex with free ethylene added.
Resonances: (A) axial ethylene, (B) equatorial ethylene, (C) free ethylene, (D) merged resonance of free and equatorial ethylene.

intensity ratio 1 : 3 at τ = 8.39 ppm (A) and at 6.49 ppm (B) due to the axial and equatorial ethylene ligands*). The

*) The width of resonance B is highly dependent on the purity of the compound

sharpness of the resonances indicates the absence of exchange processes between axial and equatorial ethylene on the NMR time scale.

Intramolecular exchange processes are quite common in penta-coordinated compounds as $Fe(CO)_5$, PF_6, RPF_4 and AsF_5 (ref. 12) and were recently also reported (13) to occur in the penta-coordinated cyclooctadiene(COD)-iridium(I) complexes of the $RIr(COD)P_2$ type with R = alkyl and P = phosphine. Intramolecular exchange processes in penta-coordinated compounds seem to play an important role in the catalysed isomerisation of tetragonal planar complexes (14).

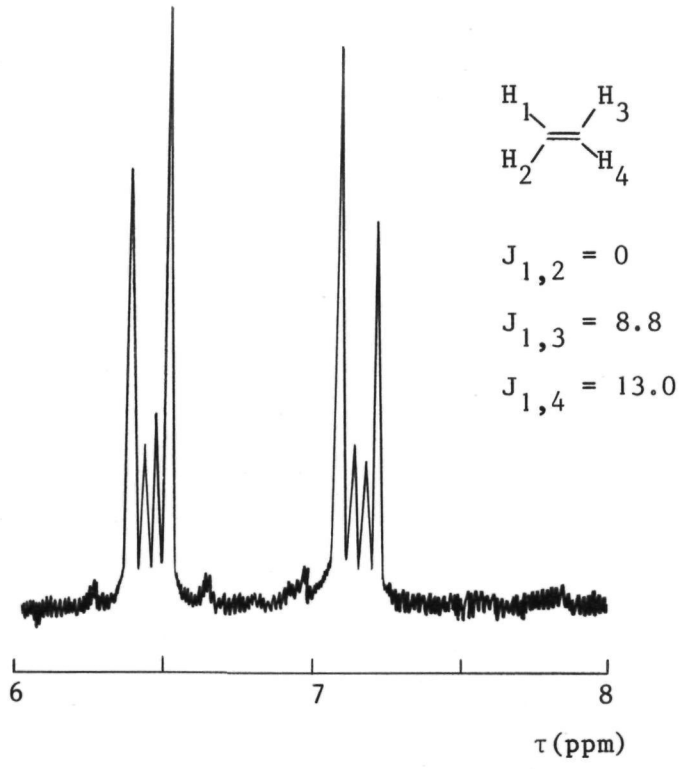


Fig. 2 Equatorial ethylene resonances in the 100 MHz spectrum of $IrCl(C_2H_4)_4$ in toluene at -60°C. Coupling constants ^2J in c/s

Although no broadening of the resonances was observed on cooling the chloroform solution, the PMR spectrum of a toluene solution at -60°C (Fig. 2), however, exhibited an AA'BB' pattern with τ_A = 6.47 and τ_B = 7.17 ppm due to the protons of the equatorial ethylene ligands. A sharp axial ethylene resonance was also observed at τ = 9.38 ppm. According to the set of proton-proton coupling constants (Fig. 2), which was obtained by spectrum simulation, the cis-protons of the equatorial ethylene ligands are equivalent in this 'frozen out' situation (16). This corresponds with an in-plane orientation of the equatorial ethylene ligands in agreement with the structure found by X-ray methods (11). Since the equatorial in-plane ethylene ligands use the metal orbitals $d_{x^2-y^2}$ and d_{xy} for π-back bonding, and the perpendicular ethylene ligands would compete with the axial ethylene ligand for the π-bonding metal orbitals d_{xz} and d_{yz}, the in-plane orientation is slightly more favourable from the point of view of π-backbonding possibilities. This alkene orientation has also been found in the trigonal bipyramidal complexes tetracarbonyl(fumaric acid)iron(0), $Fe(CO)_4(COOHCH=CHCOOH)$ (Ref. 16), and chlorotri(3-butenyl)phosphinerhodium(I), $RhCl[P(CH_2CH_2CH=CH_2)_3]$ (Ref. 17).

The different dependency on temperature of the PMR spectra of 2 in chloroform and toluene demonstrates the solvent influence on the barrier of rotation of the equatorial ethylene ligands around the metal-alkene axes. From the coalescence temperature at about -30°C and the chemical shift difference $\tau_A - \tau_B$ = 70 c/s in toluene, it seems that this barrier in toluene is of the same magnitude as those reported for rhodium(I)- (16) and platinum(II)-alkene (18) complexes (about 10-15 kcal/mole). Although the low coalescence temperature below -60°C in chloroform may be due to a small chemical shift difference $\tau_A - \tau_B$ in chloroform, it may also suggest a barrier << 10 kcal/mole. The absence of any broadening of the axial ethylene resonances in chloroform as well as in

toluene also indicates a very low barrier of rotation for this ligand.

In the solid state of 2 rotational barriers of 5.1 kcal/mole for the equatorial and 1.6 kcal/mole for the axial ethylene ligands were determined from the magnetic relaxation behaviour as a function of temperature (19). Although the σ part of the metal-alkene bond remains more or less unperturbed during the rotation, the π part of this bond is ruptured after 90° rotation and may only be replaced by another bond of π symmetry if suitable metal orbitals are available. Apart from steric effects the barrier is therefore mainly determined by the difference in π-back bonding possibilities in the equilibrium and the rotational transition state. As mentioned before, the equatorial ethylene ligands in 2 have both in the "in-plane" and in the "perpendicular" orientation possibilities for π-back bonding. The low barriers in 2 probably reflect both the small change in π-back bonding during the rotation and the competition by the four ethylene ligands for the metal electron density.

The broadening of the equatorial ethylene resonance on admission of free ethylene to the chloroform solution at -20°C and 0°C (peak C in Fig. 1b, c) indicates slow exchange with uncoordinated ethylene. No exchange between free ethylene and the axial ethylene ligand was detected. Only at 30°C (Fig. 1d) is the axial ethylene resonance broadened due to partial decomposition of the complex.

The mechanism of exchange between free and equatorial ethylene may be associative (Eq. 1) or dissociative (Eq. 2):

$$IrCl(C_2H_4)_4 + C_2H_4 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} IrCl(C_2H_4)_5 \qquad [1]$$

$$\frac{1}{\tau_c} = k_1 [C_2H_4] \qquad \frac{1}{\tau_f} = k_1 [IrCl(C_2H_4)_4]$$

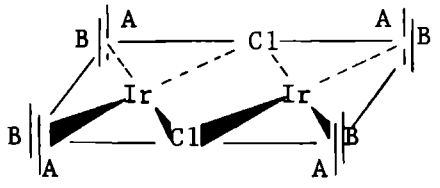
$$IrCl(C_2H_4)_4 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} IrCl(C_2H_4)_3 + C_2H_4 \qquad [2]$$

$$\frac{1}{\tau_c} = k_1 \qquad \frac{1}{\tau_f} = k_1 \frac{[IrCl(C_2H_4)_4]}{[C_2H_4]}$$

The linewidth of the resonances of the equatorial and the free ethylene ligands is proportional to the inverse lifetime of the corresponding species e.g. $1/\tau_c$ and $1/\tau_f$ respectively. The broadening of the equatorial ethylene resonance on admission of free ethylene (Fig. 1a, b) shows that the associative process is operative. This mechanism involves a six-coordinated intermediate, like (II), in which the axial ethylene ligand has to preserve its distinct character. The existence of an intermediate containing a six-coordinated d^8 metal ion has recently also been suggested in the by $RhH(CO)_2(PPh_3)_2$ selectively catalysed hydroformylation of 1-alkenes to aldehydes (20).

The dimeric complex $[IrCl(C_2H_4)_2]_2$ (3) decomposes slowly in air at room temperature and should therefore be stored under nitrogen at -20°C. In contrast to its rhodium analogue (21) 3 is moderately soluble in solvents such as benzene, chloroform and dichloromethane, but the resulting solutions are unstable at room temperature. Both compounds, which are shown by X-ray powder diagrams to be non-isomorphous, have similar IR spectra except in the far-IR region, where the iridium complex shows two and the rhodium complex three ν(metal-Cl) bands (Table II). On symmetry grounds one expects that the occurrence of two or three bands is consistent with a planar or a bent chlorine-bridge structure respectively (22,23). So the IR spectrum suggests 3 to have a planar structure (III) in contrast to its rhodium analogue, which has been shown in agreement with its IR spectrum

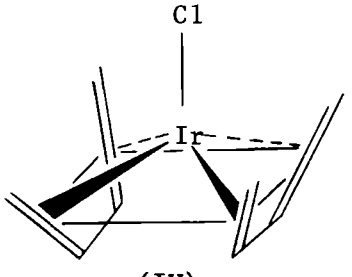
to possess a bent structure (24). Also the PMR spectrum at -55°C in chloroform, which is of the AA'BB' type with τ_A = 6.40 and τ_B = 7.79 ppm, is consistent with the planar structure (III).



(III)

The proton-proton coupling constants found by spectrum simulation ($J_{AA'}$ = 8.4; J_{AB} = 0; $J_{AB'}$ = 12.5) are not much different from those of the equatorial ethylene ligands in 2 and those of earlier reported rhodium-ethylene complexes (15). At higher temperatures, the resonances are broadened and at about 10°C they converge into one absorption, corresponding with rapid proton equilibration caused by ethylene rotation around the metal-alkene bond, and/or metal-alkene bond dissociation.

The propene complex $[IrCl(C_3H_6)_2]_2$ (4), obtained as an oil by alkene substitution in 3, shows in its IR spectrum two ν(Ir-Cl) bands centered at 290 and 255 cm^{-1} (Table II). The broadness of these bands precludes any conclusions with regard to the planar or bent nature of the metal-chlorine bridge in this dimer.



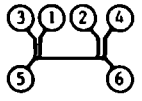
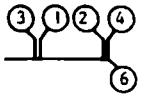
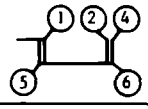
(IV)

(b) Acyclic conjugated diene complexes

The penta-coordinated monomeric complexes 5a/b, 6a/b and 7a of the type $IrX(alk)_2$ (X = Cl, Br; alk = butadiene, isoprene and 1,3-trans-pentadiene) show structure IV. All the far-IR spectra (Table II) of the chloro complexes show an absorption band in the 278-290 cm^{-1} region, which, being absent in the spectra of the bromo compounds is assigned to ν(Ir-Cl). The PMR spectra of 5a-7a (Table III) show complex resonances corresponding with the three types of olefinic protons and the methyl protons in the substituted butadiene compounds. The spectrum of the isoprene compound 6a indicates the presence of two isomeric forms (ratio $\approx$ 4 : 1) which differ in the relative position of the methyl groups. From the point of view of steric hindrance it is probable that the predominant form (A) has the methyl groups trans to each other.

Table III

PMR data (τ in ppm, J in c/s) for chloro(alkene)iridium(I) complexes in $CDCl_3$

Compound		τ_1	τ_2	τ_3	τ_4	τ_5	τ_6	τ_{CH_3}
$IrCl(butadiene)_2$		8.33		6.57		4.75		
		$J_{1,3}$ = 2.0						
		$J_{1,5}$ = 8.0		$J_{3,5}$ = 5.4				
$IrCl(isoprene)_2$	A	8.45	8.42	6.65	6.58[a]		5.31	7.95
		$J_{1,3}$ = 2.2	$J_{2,4}$ = 2.2 $J_{2,6}$ = 9.0		$J_{4,6} \approx 7$			
	B	-[b]	-[b]	-[b]	-[b]		4.83	8.24
$IrCl(1,3\text{-tr-pentadiene})_2$		7.73[c]	8.44[a]		7.20[d]	4.6-5.0[e]		8.42
		$J_{1,CH_3} \approx 6$						

a) obscured by partial overlap with CH_3 resonance

b) not located

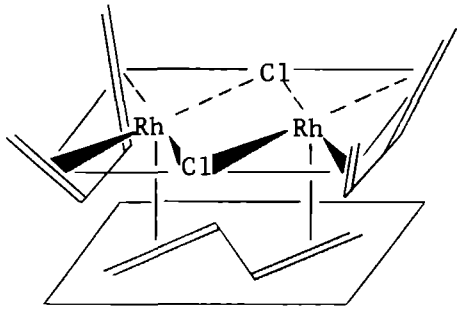
c) partly resolved quartet

d) unsymmetrical doublet

e) partly resolved multiplet

The butadiene complex 5a is far more stable in air and in solution than the earlier reported corresponding isomorphous rhodium(I) compound (25,26). This is probably due to the stronger iridium-butadiene bond which prevents alkene dissociation and formation of a reactive coordinatively unsaturated species.

This view is supported by the isolation of the dimeric complex dichlorotris(butadiene)dirhodium(I), $Rh_2Cl_2(C_4H_6)_3$ (8) and the unsuccessful attempts to prepare the corresponding iridium(I) complex.



(V)

The reaction of a suspension of $[RhCl(C_8H_{14})_2]_2$ with butadiene in absolute alcohol at 40°C gives the new complex 8. Spectroscopic data are consistent with the dimeric structure (V) which shows one bridging and two chelating butadiene ligands:

- The PMR spectrum in chloroform at ambient temperatures shows broadened resonances at τ 4.11 (2); 4.54 (4); 4.96 (4); 783 (4); 9.47 (4) ppm;

- The IR spectrum in the 1600-1300 cm^{-1} region shows four absorption bands at 1470 (sh), 1460 (m), 1428 (vs) and 1362 (s), corresponding with a chelating butadiene ligand as in $RhCl(C_4H_6)_2$, and also absorption bands of medium intensity at 1542 and 1488 cm^{-1} due to a bridging butadiene ligand;

- The ν(Rh-Cl) bands at 232 and 218 cm^{-1} support by their low position the occurrence of a combined chlorine and butadiene bridging structure (27).

The formation of 8 may be considered to proceed via butadiene dissociation followed by dimerisation and reaction of the formed dimer with a butadiene molecule.

(c) Cyclic polyene complexes

In solution 1a and 1b form with a slight excess of 1,5-cyclooctadiene (COD) dimers of the type $[IrX(COD)]_2$ with X = Cl (9a) or Br (9b). The former has been described earlier by Winkhaus and Singer (5). In pure COD the complexes of the type $IrX(COD)_2$ with X = Cl (10a) or Br (10b) are formed. The IR spectra of 9 and 10 do not show absorption bands in the 1600 cm^{-1} region from which the absence of uncoordinated double bonds may be concluded. In solution 10a and 10b dissociate and dimerise forming 9a and 9b respectively. Their IR spectra in the fingerprint region closely resemble the spectrum of the earlier reported (28) bis(COD)compound $Ir(SnCl_3)(COD)_2$, which has been shown to contain five-coordinated iridium in a distorted trigonal bipyramidal environment with four double bonds and one tin atom. The far-IR spectrum of 10a shows four strong bands below 330 cm^{-1}. The lowest at 210 cm^{-1} has no corresponding absorption in the spectrum of the bromo compound 10b and is therefore assigned to ν(Ir-Cl). On heating, 10a and 10b loose one COD ligand at 70°C and 97°C respectively, whereas 10b forms 9b on this occasion, and 10a forms a yellow isomer of 9a which has an almost identical IR spectrum.

Pure cyclooctatetraene forms with 1a or 3 the light brown coloured $[IrCl(C_8H_8)]_n$ (11). Its IR spectrum shows an absorption band at 1635 cm^{-1} indicating the presence of uncoordinated olefinic bonds as in the corresponding rhodium complex $[RhCl(C_8H_8)]_2$ (Ref. 9). The spectra of both compounds differ in several other aspects, the most important being the splitting of the characteristic cyclooctatetraene bands in the range

1300-1400 cm^{-1} and near 800 cm^{-1}, and the complex pattern consisting of four bands at 333, 307, 280-270 (broad, asymmetric) and 227 cm^{-1} (broad) in the ν(Ir-Cl) range. The spectrum of the rhodium compound has only two strong absorption bands in this range at 282 (s) and 257 (s), indicative of a planar bridged structure. Because of its insolubility and its complicated far-IR spectrum we conclude that 11 has a polymeric structure.

The structure of 11 is broken down in the reaction with pyridine which results in the formation of the complex $IrCl(C_8H_8)(pyr)$ (12) to which we assign a square planar structure. The PMR spectrum shows, together with the resonances due to pyridine, two equally intense resonances due to the protons of the eight-membered ring: a sharp singlet at τ = 4.33 ppm and a broadened resonance at τ = 5.84 ppm, correlating with the protons of the uncoordinated and coordinated alkenic bonds respectively. The IR spectrum shows, in agreement with the proposed structure, a band at 1626 cm^{-1} assignable to the C=C stretching frequency of an uncoordinated double bond.

(d) Bond strengths

Metal-chlorine. From the comparison of the far-IR spectra of the chloro and bromo compounds given in Table II, the iridium-chloro stretching vibrations could be assigned. Some ν(M-Cl) bands have a shoulder on the low-frequency side which is due to the occurrence of the ^{37}Cl isotope. As noted before the number of ν(M-Cl) bands in the spectra of chlorine-bridged complexes is indicative of a planar or bent structure (22,23). For instance, from the occurrence of two ν(Ir-Cl) absorption bands, at about 290 and at about 260 cm^{-1}, we may conclude that the bridged ethylene (3) and COD (9a) complexes possess a planar chlorine bridge. Comparison of the data for the chloro-rhodium and chloro-iridium complexes, and especially those of

the isomorphous bis(butadiene) compounds, demonstrates the stronger iridium-chlorine bond.

Metal-alkene. The relative strength of the metal-alkene bond in rhodium(I) and iridium(I) compounds is a controversial subject. Winkhaus and Singer (5) found the iridium-alkene compounds less stable than the rhodium analogues. They explained this by the more diffuse character of the atomic orbitals in the valence shell of iridium, and the consequently smaller overlap in the metal-alkene bond in the iridium compounds. This argument is in conflict with the values of overlap integrals calculated by Brown and Fitzpatrick (29), using the analytical functions of Basch and Gray for the metal orbitals.

In the far-IR spectra of COD complexes of the formula $[MCl(COD)]_2$ (M = Rh or Ir), evidence for stronger metal-alkene and metal-chlorine bonds in the iridium compound was found (22). Since free cyclooctadiene itself absorbs in the far-IR region, possible interference between internal-ligand and metal-ligand vibrations renders the conclusion tentative. Since the frequency of the lowest vibration in free ethylene (30) at 810 cm^{-1} is well above the region of the metal-ligand vibration frequencies at $\sim$ 550 cm^{-1}, the effect of this kind of interference may be supposed to be negligible in transition metal-ethylene complexes.

Analogous to Hiraishi's interpretation (31) of the IR spectrum of Zeise's salt, $K[PtCl_3(C_2H_4)]\cdot H_2O$, we assign the 537 cm^{-1} and 448 cm^{-1} bands in the spectrum of 3 and the 502 cm^{-1} and 398 (407 sh) cm^{-1} bands in the spectrum of the corresponding dimeric rhodium-ethylene compound to the assymetric and symmetric metal-alkene stretching frequencies.

In spite of the difference in bridge structure in both compounds, the above data allow the conclusion that the iridium-alkene bond is stronger than the rhodium-alkene bond. Also the data of the complexes of the higher alkenes indicate, despite

the possibility of interference, a stronger iridium-alkene bond.

In view of the stronger iridium-chlorine bond, having mainly σ-character, it is probable that the stronger iridium-alkene bond is caused by increased σ-donation as well as by increased π-backbonding. The far-IR spectra of corresponding chloro and bromo compounds show absorption bands at slightly lower frequencies in the latter and suggest therefore equal or slightly weaker metal-alkene bond strengths in the bromo compounds. However, the higher dissociation temperature of the bromobis(COD) compound 10b as compared with that of the corresponding chloro compound 10a is in favour of a stronger metal-alkene bond in the bromo compound. This behaviour is also in agreement with the greater tendency of bromo compounds to form penta-coordinated complexes (32) and with the consequently greater trans-influence of the bromo ligand.

Acknowledgement

We thank Professor A. van der Avoird for his stimulating interest, Messrs. D. Frost, J. Barzilay and H.J. van Reeven for making the measurement and simulating the PMR-spectra, Mr. M.A. van Schaik for taking the X-ray powder photographs and Miss M.W. Langelaan for her assistance in the synthetic part of this subject.

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CHAPTER 4

ETHYLENE REORIENTATION IN SOLID CHLOROTETRAKIS (ETHYLENE)IRIDIUM(I)*)

K. van Putte and A. van der Ent

Summary

The proton spin-lattice relaxation behaviour of solid chlorotetrakis(ethylene)iridium(I) has been investigated between liquid nitrogen and room temperature.

The results can be explained by 180^{o}-flip reorientations about the metal ligand axes. The activation energy determining the reorientation of the axial ethylene ligand is 1.6 kcal/mol and the one of the equatorial ethylene ligands is 5.3 kcal/mol.

Introduction

The temperature dependence of PMR spectra of rhodium(I) (1,2) and platinum(II) (3,4) alkene complexes is consistent with an intramolecular reorientation process involving rotation of the alkene ligand around the metal-alkene bond. On the basis of the Dewar, Chatt, Duncanson model (5,6) of the transition metal-alkene bond one might expect that especially the breaking of the π-component of this bond during rotation is responsible for the value of the barrier to rotation. The reported values from 10-15 kcal/mol, however, would seem to indicate that this barrier is rather intensive towards electronic and steric effects. Recently

*) Accepted for publication in Inorganic Chimica Acta

Cramer and Mrowca (7) reported the impossibility to freeze out on the NMR time scale the rotation of coordinated ethylene in $(\pi\text{-}C_5H_5)Rh(C_2H_4)_2.HgCl_2$ at -70°C. They interpreted this in terms of a rotation barrier lower than 10 kcal/mol.

We found the same behaviour of coordinated ethylene in $IrCl(C_2H_4)_4$ (Ref. 8) and Ir(acetylacetonato)$(C_2F_4)(C_2H_4)$ (Ref. 9). The PMR spectrum of $IrCl(C_2H_4)_4$ in chloroform shows at -20°C and -50°C sharp resonances in the ratio 1 : 3. The spectrum is consistent with a trigonal bipyramidal molecular structure with one axial and three equivalent equatorial, fast-rotating, ethylene ligands.

We now report the value of the barriers to reorientation of axial and equatorial ethylene in solid $IrCl(C_2H_4)_4$ by nuclear magnetic relaxation measurements.

Experimental

The spin-lattice relaxation measurements were performed on a Bruker pulse spectrometer, type BKr 304s, using the null method (11). The measuring frequencies were 60 and 15 MHz and the lengths of the 90° and 180° pulses were 2 and 4 μs respectively. The measurements below -50°C were carried out under vacuum, above this temperature under d_0- or d_4-ethylene.

$IrCl(C_2H_4)_4$ was prepared as described previously (8). The partly deuterated sample was prepared on the vacuum line.

After the relaxation measurements the sample was allowed to decompose to the chlorobis(ethylene)iridium(I) dimer, which in its turn was treated with excess triphenylphosphine. The d_4-ethylene contents in the obtained gas samples were determined by mass-spectrometry to be 44 and 46%.

Results and discussion

The spin-lattice relaxation behaviour is caused by time-dependent magnetic dipole-dipole interactions. It can be investigated by the measurement of the magnetization recovery curve, which shows the falling off with time of the magnetization after a radio frequency pulse. Due to fast spin diffusion caused by strong spin-spin interactions the spin-lattice relaxation behaves exponentially. The characteristic spin-lattice relaxation time T_1 is given by (12):

$$\frac{1}{T_1} = \sum_i \alpha_i C_i \left\{ \frac{\tau_{c_i}}{1 + \omega_o^2 \tau_{c_i}^2} + \frac{4 \tau_{c_i}}{1 + 4 \omega_o^2 \tau_{c_i}^2} \right\} \qquad [1]$$

where ω_o the Larmor precession frequency and τ_{c_i} the correlation time of motion i of the protons relative towards each other. τ_{c_i} is related to the activation energy (E_i^{act}) by:

$$\tau_{c_i} = \tau_{c_{oi}} \ell^{-E_i^{act}/RT} \qquad [2]$$

The value of the relaxation efficiency parameter c_i depends on the change in dipole-dipole interaction during motion i, α_i is the portion of protons involved in this motion. If the several τ_{c_i} differ considerably from each other, each motion i correlates, according to Eq. [1], with a T_1-minimum proportional to ω_o at $\omega_o \tau_{c_i} = 0.616$.

The experimental ln T_1 versus 1/T curve (Figure 1) shows two minima, indicating two motions with different correlation times by which relaxation takes place. At 60 MHz, the minimum T_1 values are 270 ms at 84°K and 93 ms at 263°K. This latter minimum becomes 24.5 ms at 232°K for 15 MHz as measuring

frequency. This demonstrates, in accordance with Eq. [1], the proportionality of T_1 with ω_o.

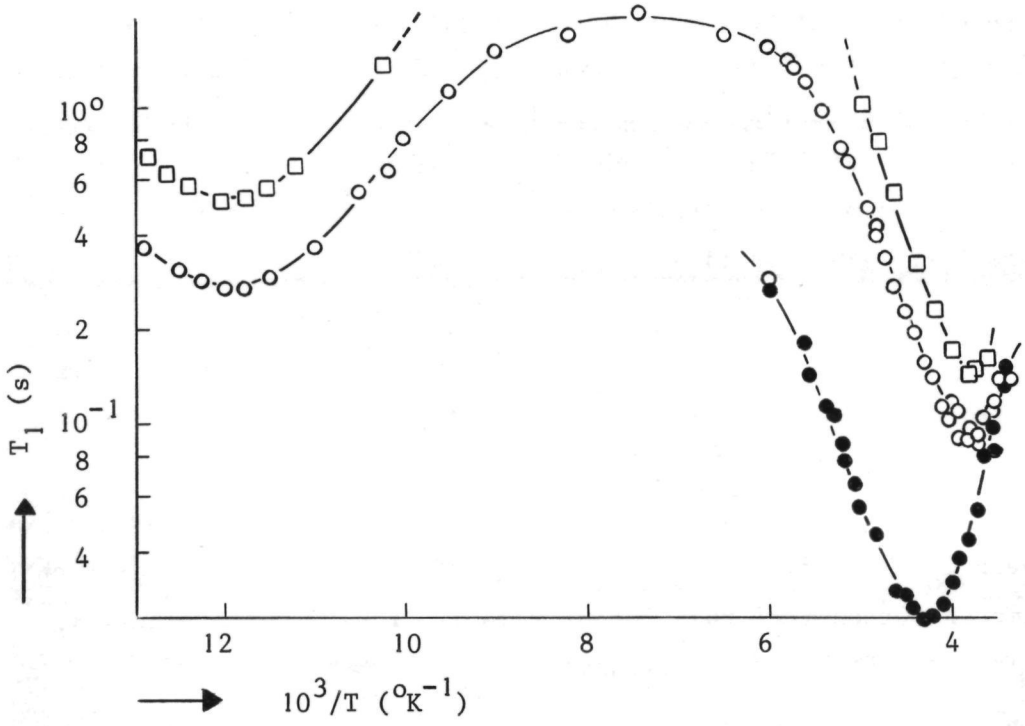

Fig. 1 T_1 as a function of inverse temperature for $IrCl(C_2H_4)_4$ (○) at 60 MHz; (●) at 15 MHz; (□) 45% deuterated at 60 MHz.

These results can be explained if we assume the axial ethylene ligand to function in the low-temperature region as a spin-lattice relaxation sink for all protons whereas the three equatorial ethylene ligands function as relaxation sinks for all protons in the high temperature region. The T_1-minima ratio found (i.e. 3) reflects the ratio of relaxing protons per relaxation sink in the low- and high-temperature region. The slope of the spin-lattice relaxation curve yields the activation energy E^{act}, corresponding with the reorientation process. E^{act} for the reorientation process of the axial ethylene ligand is 1.6 $\pm$ 0.1 kcal/mol and the one of the equatorial ethylene

ligands as calculated from the slope in the high-temperature range of the T_1 curve at 15 MHz is 4.9 $\pm$ 0.2 kcal/mol. E^{act} can also be calculated from the difference in temperature at which the T_1 minimum occurs at different measuring frequencies. E^{act} thus calculated, yields 5.3 $\pm$ 0.2 kcal/mol for the equatorial ethylene ligands, which agrees with the one found from the slope of the T_1 curve. Replacement of 45% of the ethylene ligands by deuterated ethylene resulted in an increase of both T_1 minima at 60 MHz by a factor $\approx$ 1.8. This indicates that the spin-lattice relaxation efficiency parameters c_i are largely determined by interactions between protons on different ethylene ligands. Linear extrapolation of this dilution experiment to complete deuteration yields at 60 MHz for an isolated reorienting equatorial ethylene ligand a T_1 minimum of 0.6 $\pm$ 0.1 s and for an isolated axial ligand at T_1 minimum much larger than 0.6 s.

The large difference between the inter and intra contribution to the relaxation rules out the explanation that oscillations around the metal-alkene axes over small angles ($< 20^{o}$) are responsible for the relaxation process. In this case contributions of comparable magnitude are to be expected.

In case of a pure 180^{o}-flip process around the metal-alkene axis no intra ethylene spin-lattice relaxation takes place (13). The relaxation of the axial ligand, the $T_{1\ intra}$ minimum being $>>$ 0.6 s, may well be explained by such a process. Since the symmetry of the equatorial coordination plane is 3-fold it must be concluded that this process is determined by the interactions of the axial ethylene ligand with its square intermolecular environment formed by four chlorine atoms (11) So the intramolecular barrier to rotation of this ligand will even be less than the measured value of 1.6 kcal/mol. The relaxation of the equatorial ethylene ligands can be caused either by a 180^{o}-flip process around the metal-alkene axis with a finite lifetime in a transition state or by a reorientation of the whole equatorial plane

around the molecular axis with jumps over large angles. In the latter case jumps over 60^{o} would cause dynamic disorder in the crystal structure. The occurrence of disorder, whether static or dynamic was demonstrated by X-ray investigations (10). However, such a process would not result in the earlier mentioned averaging of the equatorial protons in the high resolution spectrum. We therefore prefer the interpretation of 180^{o}-flip rotations around the metal-alkene axis to explain the relaxation behaviour of equatorial ethylene ligands.

During rotation the σ part of the metal-alkene bond remains more or less unperturbed. The π part, in contrast, is ruptured during rotation and is only replaced by another bond of π symmetry if suitable metal orbitals are available in the transition state. This is the case in four-coordinated square planar and five-coordinated trigonal bipyramidal complexes. Apart from steric effects the barrier is therefore mainly determined by the difference in π backbonding in the equilibrium and transition states. The low barriers to rotation in $IrCl(C_2H_4)_4$ are well below the region of 10-15 kcal/mol found in rhodium(I) and platinum(II) alkene complexes. The main reason may well be the absence of ligands with sufficient π-bonding capacity from the latter. In $IrCl(C_2H_4)_4$ the four ethylene ligands are competing for the metal electron density. During the rotation flip of one of the ethylene ligands the other ones may act as electron sinks to and from which the metal electron density shifts.

Acknowledgement

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CHAPTER 5

TETRAFLUOROETHYLENE COMPLEXES OF IRIDIUM(I)*)

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Summary

The chlorobis(ethylene)iridium(I) dimer, $[IrCl(C_2H_4)_2]_2$, and acetylacetonatobis(ethylene)iridium(I), $Ir(acac)(C_2H_4)_2$, react with C_2F_4 to give mixed ethylenetetrafluoroethylene complexes, in which the ethylene ligand may be replaced by alkenes such as cyclooctene and 1,5-cyclooctadiene. A number of neutral ligands can be added to these complexes with or without alkene substitution.

In several complexes a strong IR-absorption in the region 1350-1500 cm^{-1} is found and attributed to the (C=C)-stretching vibration of the fluoro-alkene. From PMR-experiments with $Ir(acac)(C_2H_4)_2$ and $Ir(acac)(C_2H_4)(C_2F_4)$ it could be concluded that the rate of associative ethylene exchange and the barrier to rotation around the metal-ethylene bond were related to the basicity of the metal substrate. The process of alkene addition is discussed in terms of nucleophilic attack of the metal on the empty antibonding alkene-orbitals.

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Introduction

The coordination chemistry of tetrafluoroethylene is characterized by the relatively low addition rate of the alkene to transition metals and the rigid three-membered ring structure of the metal-tetrafluoroethylene moiety in the resulting complexes (1-12). Generally the C_2F_4-complexes differ from their C_2H_4-analogues in the stronger metal-alkene bond, in the absence of alkene rotation around this bond together with better coordination properties towards Lewis bases.

In addition to the high basicity of iridium(I) and its ability to form penta-coordinated complexes, these features made a study of iridium(I)-tetrafluoroethylene complexes worthwhile. Some iridium-tetrafluoroethylene compounds have been reported earlier (1,2,12,13). This paper deals with the preparation and characterization of chloro- and acetylacetonato-iridium(I)-alkene-tetrafluoroethylene complexes and their behaviour towards Lewis bases.

Experimental Section

IR-spectra were recorded on the Hitachi spectrometers EPI-G2 (4000-400 cm^{-1}) and EPI-L (700-200 cm^{-1}) in KBr disks and as Nujol mull between CsI disks respectively. PMR spectra were recorded on a Varian A-60 MC spectrometer and ^{19}F NMR spectra on a Varian HA-100 MC spectrometer adapted with a 94.1 MC external oscillator. The magnetic saturation measurements were performed at 60 MC on a Bruker Kernspinrezonanz-Impuls spektrometer B-KR 3045. Melting points were measured on a Reichert hotstage microscope and are uncorrected. Microanalyses and molecular weight determinations were performed by Dr A. Bernhardt, Mikroanalytisches Laboratorium, Elbach über Engelskirchen, Germany.

Table 1. Preparation and analytical data of chloro-iridium(I)-alkene-tetrafluoroethylene complexes.

	Compound	Starting from	Procedure
1b	$[IrCl(C_2H_4)(C_2F_4)]_n$	$IrCl(C_2H_4)_4$ (0.5 g) in 15 ml ethylene-saturated dry ether.	Stir mixture at -20°C under C_2F_4 for 20 min, remove solvent under reduced pressure.
1c	$[IrCl(C_8H_{14})(C_2F_4)]_n$	$[IrCl(C_8H_{14})_2]_2$ (1.0 g) in 25 ml dry ether.	Pass ethylene through with simultaneous cooling to -70°C for 5 min, stir under C_2F_4 at -20°C for 20 min, remove solvent under reduced pressure, wash with cold alcohol, dry under vacuum.
3	$[IrCl(C_8H_{12})(C_2F_4)]_2$	$[IrCl(C_8H_{14})(C_2F_4)]_n$(0.5g) in 15 ml ether.	Add 0.5 ml 1,5-cyclooctadiene and stir for a few minutes, filter off precipitate and wash with ether.
5	$[IrCl(PPh_3)(C_2F_4)]_2$	$[IrCl(C_8H_{14})(C_2F_4)]_n$ (0.350 g) in 15 ml pentane.	Add under vigorous stirring 0.208 g PPh_3 in 25 ml pentane, filter off precipitate and wash with pentane
6	$IrCl(PPh_3)_2(C_2F_4)$	$[IrCl(C_8H_{14})(C_2F_4)]_n$ in 25 ml pentane.	Add under vigorous stirring 0.45 g PPh_3 in 25 ml CH_2Cl_2, filter solution, concentrate to 5 ml, cool to -70°C filter off precipitate, wash with pentane, recrystallize from a pentane-CH_2Cl_2 mixture.
7	$IrCl(AsPh_3)_2(C_2F_4)$	See 6.	See 6 but recrystallize twice
9a	$[IrCl(C_2H_4)(C_2F_4)(CH_3CN)]_n$	Cold solution of 1b, prepared in situ from $IrCl(C_2H_4)_4$ and C_2F_4 in ether.	Add CH_3CN dropwise, filter off precipitate, wash with ether and pentane.
9b	$[IrCl(C_8H_{14})(C_2F_4)(CH_3CN)]_n$	Solution of 1c in pentane.	Add CH_3CN dropwise, filter off precipitate, wash with pentane.
10	$IrCl(C_8H_{14})(C_2F_4)(py)_2$	1c dissolved in minimum of pyridine.	Add pentane after 30 min, filter off precipitate and wash with pentane
11a	$IrCl(C_2H_4)(C_2F_4)(dipy)$	Solution of 1b prepared in situ.	Add 2,2'-dipyridyl under vigorous stirring, filter off precipitate and wash with alcohol.
11b	$IrCl(C_8H_{14})(C_2F_4)(dipy)$	1c (0.350 g).	Stir with 2,2'-dipyridyl in ether, filter off precipitate and wash with alcohol.
12a	$Ir(NH_3)_3(C_2H_4)(C_2F_4)^+ Cl^-$	1b prepared in situ.	Pass dry NH_3 through for 20 min, filter off precipitate and wash with ether.
12b	$Ir(NH_3)_3(C_8H_{14})(C_2F_4)^+ Cl^-$	Acetone solution of 1c.	See 12a
13	$IrCl(C_8H_{12})(C_2F_4)(py)$	3 dissolved in minimum of pyridine	See 10

a) osm. in acetone; b) osm. in benzene; c) osm. in chloroform; d) osm. in methanol

Yield (%)	Elementary analysis calculated / found					M.P. °C	Mol. wt. calculated / found	Properties
	C	H	F	Cl/O/S	N/P/As			
								Unstable, can be stored at -20°C under argon for 1 month.
80	27.3 29.4	3.2 3.5	17.4 17.1	8.1 8.0		dec.	438 1110[b] 2450[a]	Yellow, store under vacuum at -20°C.
90	27.6 29.3	2.8 3.5	17.5 17.0	8.2 7.9		143-147 (dec.)	436 756[c]	Yellow, airstable.
88	40.7 40.3	2.5 3.1	12.9 12.5	6.0 5.8	5.3 5.0	dec.	1180 1150[a]	Yellow
55	53.6 53.6	3.6 3.8	8.9 9.1	4.2 4.2	7.3 7.2	222-223 (dec.)	852 870[b]	Yellow
30	48.5 50.2	3.2 3.7	8.1 8.0	3.8 3.8	16.0 15.7	190-198	940 956[b]	Yellow
80	18.1 18.3	1.8 1.6	19.1 19.4	8.9 7.4	3.5 3.6	dec.		White
75	30.1 30.2	3.6 3.7	15.9 16.0	7.4 7.5	2.9 3.1	dec.		Pale-yellow
70	40.3 40.4	4.0 4.5	12.8 12.9	6.0 5.8	4.7 4.8	dec.	594 583[b]	White
76	32.8 33.0	2.3 2.4	14.9 15.0	6.9 7.1	5.5 5.3	dec.		White
85	40.4 40.4	3.7 3.9	12.8 12.9	6.0 5.8	4.7 4.8	dec.		White
85	11.8 12.0	3.2 3.2	18.7 18.9	8.7 8.7	10.3 10.5	dec.	407 276[d]	White
89	24.6	4.7	15.5	7.3	8.6	92-96 (dec.)	489 260[d]	White
72	35.0 36.2	3.3 3.5	14.8 14.6		2.7 2.8	dec.		White

Table II. Preparation and analytical data of acetylacetonato-iridium(I)-alkene-tetrafluoroethylene complexes.

	Compound	Starting from	Procedure
2a	$Ir(acac)(C_2H_4)_2$	$IrCl(C_2H_4)_4$ (0.70 g) in 20 ml peroxide-free ethylene-saturated tetrahydrofuran.	At -80°C add acetylacetone (0.3 g), add powdered KOH (0.2 g) and stir for 30 min on an ice-bath, add 30 ml H_2O, filter off precipitate and wash with water and alcohol.
2b	$Ir(acac)(C_2H_4)(C_2F_4)$	2a (0.80 g) in 20 ml pentane.	Treat with C_2F_4 for 20 min, concentrate solution under ethylene cool to -70°C, filter off precipitate, wash with pentane and recrystallize from ether.
2c	$Ir(acac)(C_8H_{14})(C_2F_4)$	2b (1.30 g) in pentane.	Add C_8H_{14} (0.40 g), remove ethylene by a stream of nitrogen concentrate, cool to -70°C, filter off precipitate in the cold and recrystallize from ether.
4	$Ir(acac)(C_8H_{12})(C_2F_4)$	2b (0.40 g).	Add 2b to C_8H_{12} (0.120 g) in 10 ml pentane, cool after stirring to -70°C, collect crystals on filter.
14	$Ir(acac)(CO)(C_2F_4)$	2b in pentane.	Pass CO through, replace after a few min CO by nitrogen till a few ml of solvent are left, filter off precipitate and wash with pentane.
15	$Ir(acac)(PPh_3)(C_2F_4)$	2b in pentane	Add excess PPh_3, filter off precipitate and wash with pentane.
16	$[Ir(acac)(C_2F_4)(CH_3CN)]_n$	2b	Dissolve 2b in CH_3CN, filter off after 3 days the crystals and wash with acetone.
17a	$Ir(acac)(C_2H_4)(C_2F_4)(py)$	2b in pentane.	Add pyridine slowly filter off precipitate, wash with pentane and recrystallize from CH_2Cl_2.
17b	$Ir(acac)(C_8H_{14})(C_2F_4)(py)$	2c in pyridine.	After standing overnight add pentane, filter off precipitate and wash with acetone.
18a	$Ir(acac)(C_2H_4)(C_2F_4)(NH_3)$	2b in acetone.	Pass through NH_3, filter off precipitate and wash with acetone.
18b	$Ir(acac)(C_8H_{14})(C_2F_4)(NH_3)$	2c in acetone.	See 18a.

a) osm. in acetone; b) osm. in benzene; c) osm. in chloroform;
d) second m.p. 155-157°C; e) second m.p. 130-135°C.

Yield (%)	Elementary analysis calculated / found					M.P. °C	Mol. wt. calculated / found	Properties
	C	H	F	Cl/O/S	N/P/As			
92	31.1 31.0	4.3 4.4		9.2 9.4		⟩ 120 (subl. dec.)	347 388[b]	Orange
75	25.8 25.8	2.6 2.7	18.1 20.5			114-115 (dec.)	419 446[b]	Yellow
80	35.9 38.4	4.2 4.4	15.2 15.4			131-133	501 541[b]	Yellow
63	36.1 36.2	3.8 3.7	15.2 17.9			116-120[d]	499 515[c]	Yellow
85	22.9 24.1	1.7 1.8	18.1 19.1			dec.	419 445[a]	Pale-rose
90	56.4 57.3	4.0 4.3	8.3 7.7	6.8 6.2		195-198	915 902[c]	Yellow
30	25.0 26.2	2.3 2.3	17.6 18.6	3.2 3.5		dec.		Pale-yellow
78	33.7 33.5	3.2 3.3	15.3 15.7	2.8 3.2		dec.		White
89	41.4 41.4	4.5 4.4	13.1 13.9	2.4 2.7		127-131	580 450[b]	White
85	24.8 23.9	3.2 3.3	17.5 19.8			dec.		White
82	34.8 34.6	4.6 4.8	14.6 15.7	2.7 3.0		81-86[e]	518 481[b]	White

Materials: $(NH_4)_3IrCl_6$ was purchased from Messrs. Drijfhout, Amsterdam. $IrCl(C_2H_4)_4$ and $[IrCl(C_8H_{14})_2]_2$ were prepared by literature methods (14). C_2F_4 was prepared by cracking teflon-fibres at 500-550°C under vacuum. Subsequently it was passed over KOH pellets and condensed in a nitrogen trap. Solid and gaseous reagents were used without purification; solvents were reagent-grade, degassed with nitrogen before use, and if required dried over sodium.

Reactions were carried out under nitrogen or ethylene. Whenever possible, working up of the products was done in air. The preparation and analytical data of the complexes prepared are given in Tables I and II.

PREPARATION AND CHARACTERIZATION OF ALKENE-TETRAFLUOROETHYLENE IRIDIUM(I) COMPLEXES

Chloro-complexes

Although C_2F_4 generally reacts rather slowly with transition metal complexes, its reaction with the bis(ethylene) complex $[IrCl(C_2H_4)_2]_2$ (1a) (Ref. 14) in ether or pentane at -20°C is complete within 20 min giving the yellow $[IrCl(C_2H_4)(C_2F_4)]_n$ (1b). At room temperature 1b degradates readily to ill-defined carbonyl-compounds under the influence of atmospheric moisture. A similar behaviour has also been found with other C_2F_4-complexes (12). The compound can be stored at -20°C under argon for over a month without much decomposition. Solutions are unstable, even at low temperature. Its instability obstructs normal analysis and molecular weight determination. A freshly prepared sample was destroyed with KOH and H_2O_2 and the Cl/F ratio in the resulting mixture was determined as 1.00 : 4.10. Magnetic saturation measurements at -50°C showed that 12.8 ± 1.3 mmole H and 10.4 ± 0.9 mmole F per g were present (theoretical 11.3 mmole H and F per g).

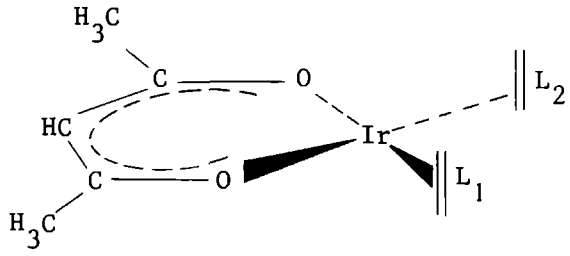
The chemical behaviour of 1b towards Lewis bases, described in the next section, also confirmed its composition.

C_2F_4 does not react with the chlorobis(cyclooctene)-iridium(I)-dimer, $[IrCl(C_8H_{14})_2]_2$(Ref. 14), but cyclooctene displaces ethylene from 1b to give the yellow $[IrCl(C_8H_{14})(C_2F_4)]_n$ (1c). The reaction can be carried out in situ, by treating a suspension of $[IrCl(C_8H_{14})_2]_2$ in ether or pentane with C_2H_4 and C_2F_4 successively. 1c is very similar to 1b but is somewhat more stable. As indicated by molecular weight measurements, 1c is associated in solution, n being about $2\frac{1}{2}$ in benzene and about $5\frac{1}{2}$ in acetone.

Both 1b and 1c give with 1,5-cyclooctadiene in ether the yellow, airstable compound $[IrCl(C_8H_{12})(C_2F_4)]_2$ (3). This compound is only slightly soluble in methanol and chloroform. Its molecular weight in the latter solvent indicates a dimeric structure.

Acetylacetonato complexes

The monomeric acetylacetonatobis(ethylene)iridium(I), $Ir(acac)(C_2H_4)_2$, (2a) was prepared as an orange precipitate by



I (compounds: 2a $L_1=L_2=C_2H_4$;
2b $L_1=C_2H_4, L_2=C_2F_4$;
2c $L_1=C_8H_{14}, L_2=C_2F_4$)

treating a suspension of $IrCl(C_2H_4)_4$ (Ref. 14) in tetrahydrofuran below 0°C with acetylacetone and KOH, after which water was added.

2a reacts with C_2F_4 at room temperature within 20 min to give the yellow $Ir(acac)(C_2H_4)(C_2F_4)$ (2b) which is more stable than the corresponding chloro-complex 1b. The ethylene ligand in 2b can be replaced by cyclooctene and 1,5-cyclooctadiene, giving $Ir(acac)(C_8H_{14})(C_2F_4)$ (2c) and $Ir(acac)(C_8H_{12})(C_2F_4)$(4) respectively. C_2F_4 is loosely bound in 4; at the melting point this compound quickly loses all C_2F_4 and decomposes into $Ir(acac)(C_8H_{12})$(Ref. 15).

Depending on the molecular symmetry, in the PMR spectra of the acetylacetonato complexes one or two methyl-resonances may be present (see Table III). So the spectrum of 2a, showing only one methyl-resonance, indicates the presence of a plane of symmetry. As may be concluded from the present of two methyl-resonances, such a plane is absent in the structure of the monomeric complexes 2b, 2c and 4.

For the complexes $Ir(acac)(C_2H_4)_2$ (2a) and $Ir(acac)(C_2H_4)(C_2F_4)$ (2b) proton spectra, taken under various conditions are given in Fig. 1.

Although structurally similar, the compounds show striking differences. At ambient temperature 2a shows a broad ethylene-resonance at τ = 7.42 (8). At low temperature this resonance is completely resolved into a sharp AA'BB' pattern, similar to that found at low temperatures for rhodium-ethylene compounds (11,16) for which spectrum simulation proved the equivalence of the cis-protons of the C_2H_4-ligands and as a consequence the perpendicular orientation of the C=C bond to the coordination plane (Structure I). We may conclude that ethylene rotation in 2a is rather a slow process at ambient temperature and that at -50°C the 'frozen out' situation is obtained. On the other hand, 2b shows both at 40°C and -50°C only a slightly broadened single

Table III. PMR spectra of iridium(I)-C_2F_4 complexes; internal ref. TMS, 40°C, τ-values, number of protons in parentheses, solvent $CDCl_3$.

	Compound	Alkene protons	Acac protons	Other ligands
	C_2H_4	4.65		
2a	$Ir(acac)(C_2H_4)_2$	7.42(8) broad	4.51(1), 8.00(6)	
	idem at -50°C	6.86(4), 8.12(4)[d]	4.46(1), 7.99(6)	
2b	$Ir(acac)(C_2H_4)(C_2F_4)$	6.23(4)	4.29(1), 7.79(3), 7.90(3)	
	idem at -50°C	6.27(4)	4.27(1), 7.79(3), 7.93(3)	
17a	$Ir(acac)(C_2H_4)(C_2F_4)(py)$	6.18(4)	4.97(1), 8.14(6)	1.39(2), 2.32(1) 2.72(2)
18a	$Ir(acac)(C_2H_4)(C_2F_4)(NH_3)$	6.35(4)	4.85(1), 8.10(6)	
12a	$[Ir(NH_3)_3(C_2H_4)(C_2F_4)]Cl$[a]	6.53		
	C_8H_{14}	4.45(2), 7.90(4), 8.48(8)		
1c	$[IrCl(C_8H_{14})(C_2F_4)]_n$[b]	5.9(2), 7.90(4), 8.50(8)		
12b	$[Ir(NH_3)_3(C_8H_{14})(C_2F_4)]Cl$[c]	6.1(2), 8.1, 8.50(12)		
2c	$Ir(acac)(C_8H_{14})(C_2F_4)$	6.0(2), 7.8(4), 8.50(8)	4.43(1) 7.92, 7.94(6)	
17b	$Ir(acac)(C_8H_{14})(C_2F_4)(py)$	5.5(2), 8.07(4), 8.48(8)	5.17(1), 8.25(6)	1.40(2), 2.33(1) 2.83(2)
18b	$Ir(acac)(C_8H_{14})(C_2F_4)(NH_3)$	5.75(2), 8.2(4) 8.50(8)	4.80(1), 8.08(6)	
	C_8H_{12}	4.54(4), 7.70(8)		
4	$Ir(acac)(C_8H_{12})(C_2F_4)$	4.40(1), 5.17(1) 5.76(1), 6.20(1) 7.40(4), 8.00(4)	4.75(1) 7.93(3), 8.20(3)	
15	$Ir(acac)(PPh_3)_2(C_2F_4)$		4.75(1) 8.26(3), 8.55(3)	2.82, 3.02(30)
14	$Ir(acac)(CO)(C_2F_4)$		4.27(1), 7.83(3), 7.90(3)	

a) solvent D_2O, internal ref. TSS; b) solvent-acetone-d_6;

c) solvent CD_3OD; d) AA'BB' pattern, at 8.12 partially hidden under methyl resonances.

ethyleneresonance at τ = 6.23 (4). We attribute this to a fast ethylene rotation, many times faster than in the bis-ethylene complex 2a.

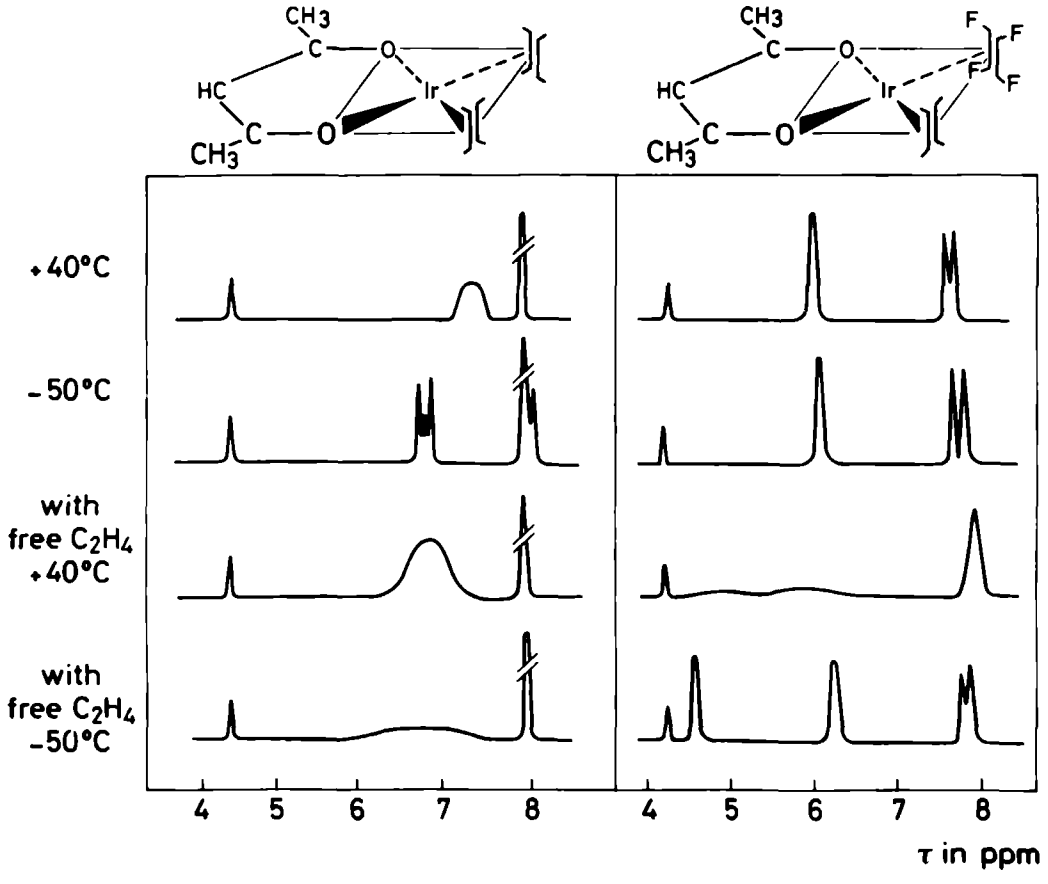


Fig. 1 PMR-spectra (diagrammatic) at 60 MC in $CDCl_3$

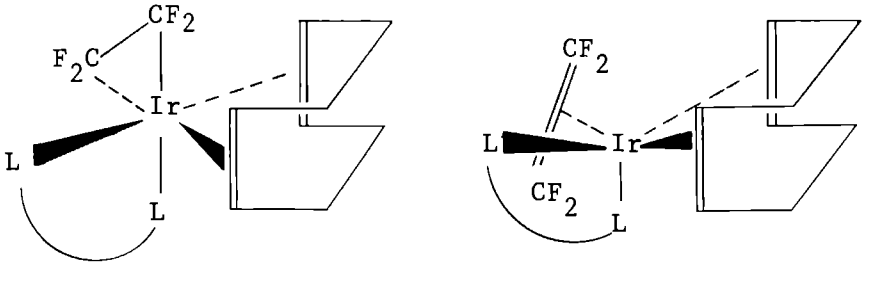
Since two distinct acetylacetonato-methyl-resonances are present in the spectrum of 2b, it is not likely that dissociation of ethylene is the cause of the fast C_2H_4-proton-equilibration. However, the latter process does occur to a certain extent in 2b as can be concluded from the sharpening at low temperature of the methyl-resonances which are slightly broadened at 40°C. Because of the stronger metal-ethylene bond in 2a, we think this process is absent in the case of this compound.

In the presence of free ethylene, 2a shows at 40°C a broad single absorption centred at τ = 6.79 (10.8), which at

$-50^{o}C$ is further broadened, ranging from about $\tau = 6.0$ to $\tau = 7.7$. 2b shows in the presence of free ethylene at $-50^{o}C$ two completely separated and rather sharp absorptions at $\tau = 4.6$ (3.4) for free and at $\tau = 6.3$ (4) for coordinated ethylene. At $40^{o}C$, these absorptions are substantially broadened, but not yet completely collapsed into one broad absorption. At this temperature, ethylene-exchange causes equilibration of the methyl groups to such an extent that only one, although broad, methyl absorption is found. The exchange proceeds by both a dissociative and an associative mechanism, although the dissociative mechanism operates only slowly, as can be seen from the slight broadening of the methyl-resonances in the absence of free ethylene. The faster associative mechanism is, however, slow compared with the same process in 2a which even at $-50^{o}C$ shows one very broad absorption due to free and coordinated ethylene.

Summarizing and comparing the properties of 2a and 2b deduced from the NMR spectra we find that 2a shows slow ethylene rotation and fast ethylene exchange, 2b on the contrary fast rotation and slow exchange.

The PMR spectrum of 4 not only shows two nonequivalent methyl-groups but also four distinct alkenic protons to be present. The ^{19}F NMR spectrum (Table IV) shows the nonequivalence of the four fluorine atoms. The structure of 4 may



A B

II (compound 4)

therefore be described either as distorted octahedral with a bidentate C_2F_4 ligand (Structure IIA) or alternatively, as tetragonal pyramidal with a monodentate C_2F_4 ligand, occupying one of the equatorial coordinates sites (Structure IIB)*).

BEHAVIOUR OF ALKENE-TETRAFLUOROETHYLENE-IRIDIUM(I)-COMPLEXES TOWARDS LEWIS BASES

Chloro-complexes

In the reaction of triphenylphosphine with $[IrCl(alk)(C_2F_4)]_n$ (1b, c) the first step is the replacement of the alkene ligand. The addition of the second phosphine involves breaking of the chlorine-bridge.

$$[IrCl(alk)(C_2F_4)]_n \text{ (1b, 1c)} \xrightarrow{PPh_3} [IrCl(C_2F_4)(PPh_3)]_2 \text{ (5)}$$

$$\xrightarrow{PPh_3} IrCl(C_2F_4)(PPh_3)_2 \text{ (6)} \xrightarrow{PPh_3} IrCl(C_2F_4)(PPh_3)_3 \text{ (Ref. 12).}$$

In a similar manner $IrCl(C_2F_4)(AsPh_3)_2$ (7) was obtained. The behaviour of 1b and 1c towards triphenylphosphine mainly parallels the behaviour of $[IrCl(C_2H_4)_2]_2$ (1a). The difference lies in the last step, which in the case of 1a involves the slow formation of $IrCl(PPh_3)_3$ by replacement of ethylene from $IrCl(C_2H_4)(PPh_3)_2$ (Ref. 17). In the reaction of $[IrCl(C_8H_{12})(C_2F_4)]_2$ (3) with

*) The structure designs in this paper are for reasons of clarity based either on square planar or on octahedral coordination of the metal with C_2F_4 consequently acting as a mono- or bidentate ligand respectively; this choice does not intend to state the bonding mode of C_2F_4. For the determination of coordination numbers C_2F_4 is always referred to as a monodentate ligand.

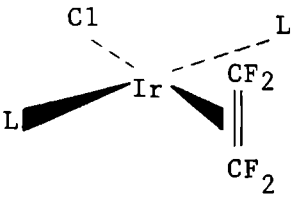
Table IV. ^{19}F NMR spectra of iridium(I)-C_2F_4 complexes; 30°C, lock external CF_3COOH

	Compound	Shift δ (ppm)	Pattern	Solvent
	C_2F_4	54.6	singlet	CH_2Cl_2
1c	$[IrCl(C_8H_{14})(C_2F_4)]_n$	35.1 51.8	broadened AB	acetone
6	$IrCl(PPh_3)_2(C_2F_4)$	22.7	apparent triplet	CH_2Cl_2
7	$IrCl(AsPh_3)_2(C_2F_4)$	20.5	singlet	CH_2Cl_2
12a	$[Ir(NH_3)_3(C_2H_4)(C_2F_4)]Cl$	53.1 55.5	broadened AB	CH_3OH
12b	$[Ir(NH_3)_3(C_8H_{14})(C_2F_4)]Cl$	51.2 59.1	broadened AB	CH_3OH
2b	$Ir(acac)(C_2H_4)(C_2F_4)$	44.5	complex	CH_2Cl_2
2c	$Ir(acac)(C_8H_{14})(C_2F_4)$	42.5 50.6	AA'BB'	CH_2Cl_2
4	$Ir(acac)(C_8H_{12})(C_2F_4)$	43.1 50.7 51.9 57.0	complex complex complex complex	CH_2Cl_2
14	$Ir(acac)(CO)(C_2F_4)$	34.4 52.5	AA'BB'	acetone
17b	$Ir(acac)(C_8H_{14})(C_2F_4)(py)$	49.3 55.7	broadened AB	CH_2Cl_2
18a	$Ir(acac)(C_2H_4)(C_2F_4)(NH_3)$	50.6 53.3	broadened AB	CH_2Cl_2
18b	$Ir(acac)(C_8H_{14})(C_2F_4)(NH_3)$	48.7 58.2	broadened AB	acetone

triphenylphosphine, a product has been obtained which showed in its IR-spectrum C_2F_4-absorptions of varying intensity, indicating the formation of $IrCl(PPh_3)(C_8H_{12})(C_2F_4)$(8), which slowly loses C_2F_4. A likewise unstable product has been obtained from the action of cyclooctadiene on 5.

The molecular weight of 5, which is only slightly soluble in alcohol and acetone, agrees with a dimeric formulation in the latter solvent. The trans-structure of 6 (see Structure III) which was described earlier by Stone et al. (12), may be concluded from its ^{19}F spectrum (Table IV). This shows an apparent triplet due to coupling of the ^{19}F spins with two strongly coupled ^{31}P nuclei ($I=\frac{1}{2}$). The ^{19}F spectrum of the corresponding arsine compound 7 shows, in agreement with the trans-structure, a single sharp resonance. The spectra of 6 and 7 are unaffected by temperature changes and by the presence of free C_2F_4. The latter indicates the absence of a C_2F_4-exchange process on the NMR time scale.

With nitrogen Lewis bases 1b and 1c generally yield addition compounds. Due to their insolubility or instability in solution these compounds, with the exception of the ammonia complexes, are not suitable for NMR investigations.



III (compounds:
6 L=PPh_3; 7 L=$AsPh_3$)

Consequently with methylcyanide the white complex $[IrCl(C_2H_4)(C_2F_4)(CH_3CN)]_n$ (9a) and the pale-yellow complex $[IrCl(C_8H_{14})(C_2F_4)(CH_3CN)]_n$ (9b) are formed. The presence of ethylene in 9a was demonstrated in the reaction with ammonia (see below).

During the reaction of 1b with a solution of pyridine ethylene is rapidly generated. The resulting product still showed C_2F_4-absorptions in the IR-spectrum, but could not be characterized. 1c yields with pyridine the penta-coordinated adduct $IrCl(C_8H_{14})(C_2F_4)(py)_2$ (10). The reaction of a pyridine solution with 1a resulted in the formation of the monomeric 1 : 1 adduct cis-$IrCl(C_2H_4)_2(py)$ (Ref. 18).

Equimolar amounts of 2,2'-dipyridyl yields with 1b and 1c the adducts $IrCl(alk)(C_2F_4)(dipy)$ (11a alk = C_2H_4 and 11b alk = C_8H_{14}). With ammonia the ionic penta-coordinated compounds $[Ir(NH_3)_3(alk)(C_2F_4)]^+ Cl^-$ (12a alk = C_2H_4 and 12b alk = C_8H_{14}) are obtained. The compounds are soluble in ionizing solvents such as alcohol and water. Their molecular weight as well as the conductivity in methanol are in agreement with their ionic character. 12a can also be prepared by substitution of the methyl cyanide ligand in 10, proving the presence of ethylene in the latter.

The cyclooctadiene compound 3 showed no reaction with methylcyanide and 2,2'-dipyridyl but with pyridine the 1 : 1 adduct $IrCl(C_8H_{12})(C_2F_4)(py)$ (13) was formed.

Acetylacetonato-complexes

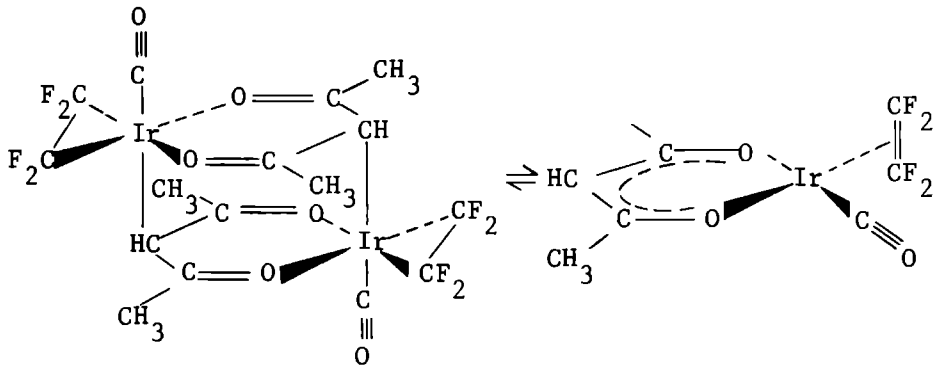
The reaction of the acetylacetonato compounds 2b and 2c with carbonmonoxide yields a pale-rose coloured compound of composition $Ir(acac)(CO)(C_2F_4)$ (14). It turns yellow in various solvents, but can be recovered unchanged from chloroform and acetone solutions by evaporating the solvent under a stream of nitrogen

Table V. Infrared data (cm^{-1})

	Compound		$\nu(C_2F_4)$		ν(acac) and others
1c	$[IrCl(C_8H_{14})(C_2F_4)]_n$	814s	1053s, 1157s	1475s	
3	$[IrCl(C_8H_{12})(C_2F_4)]_2$	785s	1053s, 1107s, 1183s	1377s, 1403s	
5	$[IrCl(PPh_3)(C_2F_4)]_2$	807s	1027s, 1096s		
6	$IrCl(PPh_3)_2(C_2F_4)$	817s	1030s, 1098s		305m ν(Ir-Cl)
7	$IrCl(AsPh_3)_2(C_2F_4)$	803s	1030s, 1110s		303m ν(Ir-Cl)
9a	$[IrCl(C_2H_4)(C_2F_4)(CH_3CN)]_n$	822s	1060s, 1121s	1403s	2280w, 2320w ν(C≡N)
9b	$[IrCl(C_8H_{14})(C_2F_4)(CH_3CN)]_n$	836s	1040s, 1107s	1375s	2280m, 2310m ν(C≡N)
10	$IrCl(C_8H_{14})(C_2F_4)(py)_2$	838s	1023s, 1045s, 1067s, 1080s	1348s	
13	$IrCl(C_8H_{12})(C_2F_4)(py)$	780s, 792sh	1037s, 1042, 1116s	1350s	
11a	$IrCl(C_2H_4)(C_2F_4)$(dipy)	851s	1037s, 1092s	1380s	
11b	$IrCl(C_8H_{14})(C_2F_4)$(dipy)	840s	1022s, 1050s, 1083s	1370s	
12a	$[Ir(NH_3)_3(C_2H_4)(C_2F_4)]^+Cl^-$	840s, 853sh	1037s, 1084s	1373s	
12b	$[Ir(NH_3)_3(C_8H_{14})(C_2F_4)]^+Cl^-$	838s	1020s, 1052s, 1064s	1345s	
2a	$Ir(acac)(C_2H_4)_2$				1536s, 1550sh, 1562sh, 1574sh
2b	$Ir(acac)(C_2H_4)(C_2F_4)$	799s	1043s, 1134s	1497m	1537s, 1562s
2c	$Ir(acac)(C_8H_{14})(C_2F_4)$	800s	1033s, 1050s, 1124s, 1140s	1481s	1534s, 1563s
4	$Ir(acac)(C_8H_{12})(C_2F_4)$	794s	1053s, 1086s, 1127s	1368s	1512s, 1573s, 1590s
14	$Ir(acac)(CO)(C_2F_4)$ (KBr)	815s	1068s, 1135s	1393s	1520m, 1620s, 2051s, 2064sh ν(C≡O)
	idem ($CHCl_3$)				1530s, 1563m, 2064s ν(C≡O)
15	$Ir(acac)(C_2F_4)(PPh_3)_2$	835s	1038s, 1080s	1356m	1516s, 1584s
16	$[Ir(acac)(C_2F_4)(CH_3CN)]_2$	842s, 860s	1022s, 1035sh	1377s	1640s
17a	$Ir(acac)(C_2H_4)(C_2F_4)$(py)	840s	1018s, 1036s, 1076s	1385s	1518s, 1575s
17b	$Ir(acac)(C_8H_{14})(C_2F_4)$(py)	838s	1038s, 1083s	1364s	1518s, 1587s
18a	$Ir(acac)(C_2H_4)(C_2F_4)(NH_3)$	850s	1003s, 1080s	1380s	1517s, 1572s, 1586s
18b	$Ir(acac)(C_8H_{14})(C_2F_4)(NH_3)$	843s, 858s	1012s, 1065s, 1099s	1380s	1522s, 1573s

s = strong, m = medium, w = week, sh = shoulder

or CO. IR-spectra of 14 in solution and in the solid state are different (see Table V). In chloroform it shows two bands at 1530 cm^{-1} (s) and 1563 cm^{-1} (m) indicative of an oxygenbonded chelating acac-group. In KBr-pellet, and as Nujol mull, however, instead of these two bands two new bands appeared at 1620 cm^{-1} (s) and 1520 cm^{-1} (m); the one at 1620 cm^{-1} may be indicative of a carbon-bridging acac-function (2). Molecular weight measurements showed the compound to be monomeric in solution. These findings suggest that the compound forms reversibly an iridium-carbon bond, being dimeric in the solid state with a carbon-bonded bridging acetylacetonato-group (Structure IV).

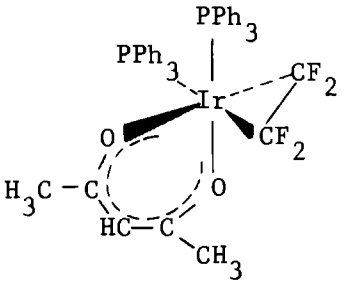


IV (Compound 14)

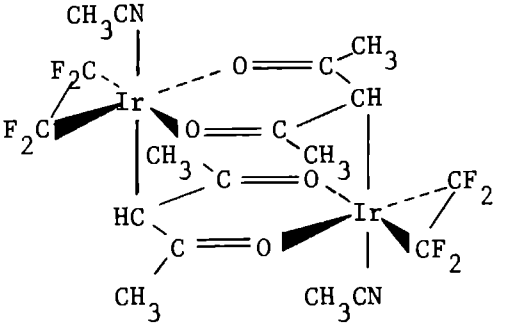
The PMR spectrum (Table III) of 14 in $CDCL_3$ shows two distinct CH_3-singlets of equal intensities, which should be expected for the monomer structure. The ^{19}F NMR spectrum (Table IV) shows a complex pattern of the AA'BB' type.

Excess triphenylphosphine yielded with 2b and 2c the yellow complex $Ir(acac)(PPh_3)_2(C_2F_4)$ (15) which, on account of the presence of two methyl-resonances of equal intensity in the PMR spectrum (Table III), has been attributed the cis-structure (Structure V). The corresponding $Rh(acac)(PPh_3)_2(C_2F_4)$ has been attributed the trans-structure on account of the presence of

only one methyl-resonance (2).



V (compound 15)

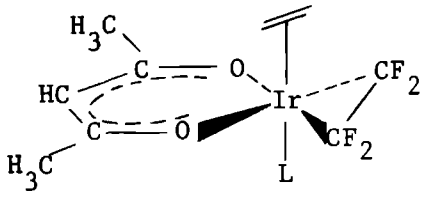


VI (compound 16)

The structure of the reaction product of 2b or 2c with methylcyanide $[Ir(acac)(CH_3CN)(C_2F_4)]_2$ (16) has been elucidated by X-ray investigation (19) by Dr van Soest of our laboratory (see Structure VI). The presence of a carbon-bridging acac-function was also indicated by a strong IR-absorption band at 1640 cm^{-1} (see Table V).

With pyridine and ammonia 2b and 2c formed pentacoordinated 1 : 1 adducts of the type $Ir(acac)(alk)(C_2F_4)L$ with alk = C_2H_4 or C_8H_{14} and L = pyridine (17) or NH_3 (18). The PMR spectra of these compounds showed only one methyl-resonance. Exchange experiments with free ethylene show that this is not caused by dissociative ethylene exchange in case of the ethylene compounds 17a and 18a. In agreement with this, the symmetrical structure VII is attributed to 17 and 18.

The bis(ethylene) complex $Ir(acac)(C_2H_4)_2$ (2a) shows a behaviour towards Lewis bases which is quite different from that of 2b. Ethylene replacement in 2a is complete with carbonmonoxide and 1,5-cyclooctadiene resulting in $Ir(acac)(CO)_2$ and Ir(acac)(diene) respectively, but no reaction with methyl cyanide and pyridine has been detected.



VII (compounds: 17a alkene = C_2H_4 and L = pyridine
17b alkene = C_8H_{14} and L = pyridine
18a alkene = C_2H_4 and L = NH_3
18b alkene = C_8H_{14} and L = NH_3)

IR-SPECTRA

In general three main regions of absorptions due to coordinated C_2F_4 are found (see Table V). Firstly, in all complexes there is a strong absorption at roughly 800 cm^{-1}, which is correlated with the symmetrical mode in free C_2F_4 at 778 cm^{-1}, which is mainly (C-F) stretching in character (20). Secondly two or three strong absorptions are found between 1000 and 1170 cm^{-1}. Thirdly most complexes show a quite intense absorption between 1340 and 1500 cm^{-1}. We connect this absorption with the (C=C) stretching vibration, which in free C_2F_4 is found at 1872 cm^{-1} in the Raman spectrum (20). Its position correlates with the basicity of the metal substrate. Thus Lewis base-adducts show this absorption 100 to 130 cm^{-1} lower than the parent complexes. Because of the electron-releasing alkyl substituents cyclooctene complexes show this absorption on an average some 15 cm^{-1} lower than the corresponding ethylene complexes. A similar lowering of the frequency on expansion of the coordination number from four to five has recently been reported for the carbonyl stretching vibration in iridium(I) and rhodium(I) complexes (21).

RATE OF BOND-FORMATION AND STABILITY OF THE METAL-ALKENE BOND

It is known that C_2F_4-coordination enhances the ability of rhodium(I) to form penta-coordinated complexes with donating ligands (1,2). The same, even to a greater extent is found with iridium(I) complexes. This influence of C_2F_4 is in agreement with the "dualistic" nature of the metal by which it acts as a base towards accepting or acidic ligands and as an acid towards donating or basic ligands (17).

The transition metal-alkene bond is generally described on the basis of the Dewar-Chatt-Duncanson model (22) in which the filled bonding σ and π orbitals of the alkene show σ-donor capacity towards empty metal orbitals and in which the empty anti-bonding σ^* and π^* alkenic orbitals can accept electron density from a filled metal orbital by overlap of π symmetry. Electronegative substituents on the alkene should increase its acceptor-properties at the expense of its donor-properties and leads to an increase in metal-alkene bond stability for complexes of electron rich metals. The influence of electronegative substituents on the rate of alkene-addition, is, however, not unambiguous. So, substitution of cyanide for hydrogen increases both the stability of the formed bond and the rate of alkene-addition (23), whereas substitution by fluorine or chlorine increases the stability but decreases the rate of addition. Since C_2F_4 was supposed to be a good π-acid, it was concluded that π-interactions played a minor role in the initial stage of the alkene-addition process (24). Molecular orbital calculations (Hückel (25) and Extended Hückel (26)) indicate, however, that interactions of the carbon p_z-orbitals with the fluor π electrons result in Higher energies of the π and π^* orbitals in C_2F_4 than in ethylene (Table VI). This would lead to higher C_2F_4-reactivities towards electrophilic and lower C_2F_4-reactivities towards nucleophilic reagents. So the low reactivity of

C_2F_4 towards transition metals can only be accounted for by a nucleophilic attack of the metal on the alkenic π^* antibonding orbitals.

Table VI. Energies of π and π^* orbitals in alkenes

Alkene	Found		Calculated[a]		
	IP (eV)	$\pi \longrightarrow \pi^*$ (cm^{-1})	π (eV)	π^* (eV)	$\pi \longrightarrow \pi^*$ (cm^{-1})
C_2F_4	10.1	71650[b]	-11.4	-3.7	62200
C_2H_4	10.5	60170[b]	-13.2	-6.3	55700
$C_2(CN)_4$		40733[c]	-13.4	-10.0	27400

a) Ref. 26; b) Ref. 27; c) Ref. 28.

The higher reactivity of tetracyanoethylene with its low lying empty π^* antibonding orbital can likewise be accounted for by the same mechanism. Also the ethylene-exchange experiments with $Ir(acac)(C_2H_4)_2$ (2a) and $Ir(acac)(C_2H_4)(C_2F_4)$(2b) combined with their chemical behaviour towards nitrogen bases contain evidence for the influence of metal-basicity on the rate of alkene-addition. The slow ethylene rotation in 2a as compared with 2b reflects the higher amount of π-backbonding from the metal to the alkene and the higher electron density on the metal. Although 2a has as a consequence a low affinity towards σ-bases, whereas 2b forms fairly stable adducts with the donor-molecules, ethyle-exchange is much faster in 2a than in 2b. So it may be concluded that nucleophilic attack of the metal on the alkene is a general feature in the addition of alkenes to transition metals.

In spite of the high π and π^* energies in C_2F_4 the direction of bond polarity is metal $\longrightarrow$ C_2F_4, as may be concluded from the enormous increase in acidity of the metal in comparison with similar ethylene complexes and from the

lowering of ν(C=C) on adduct formation with Lewis bases. This may be rationalised by the consideration that the alkene loses its planarity during the coordination process. As a consequence mixing of the alkenic π and σ orbitals occurs and the σ-inductive influence of the fluorine atoms gains importance and may become a dominant factor in determining the stability of the metal-C_2F_4 bond.

Acknowledgement

We thank Professor J.J. Steggerda and Professor A. van der Avoird, for their stimulating interest. We are grateful to Dr M. van Gorkom, Dr K.P.A.M. van Putte, Mrs H. Smeets and J. Mous for performing the NMR measurements and to Mr S. de Jong for the M.O.-calculations.

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CHAPTER 6

SOME ADDITION COMPOUNDS OF CHLOROBIS(TRIPHENYLPHOSPHINE)IRIDIUM(I)*)

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Summary

The synthesis and properties of chlorobis(triphenylphosphine)iridium(I), $IrCl(PPh_3)_2$ and some of its addition products are reported.

With ethylene, $IrCl(C_2H_4)(PPh_3)_2$ is formed. Indications have been found pointing to the formation, at low temperature, of the unstable bis(ethylene) adduct $IrCl(C_2H_4)_2(PPh_3)_2$. With one equivalent of allene, $IrCl(C_3H_4)(PPh_3)_2$ is formed. The reaction product with excess of allene is $IrCl(C_6H_8)(PPh_3)_2$, in which the 2,2'-bi-σ,π-allyl ligand is present.

In the presence of an excess of ethylene, $IrCl(C_2H_4)(PPh_3)_2$ forms with molecular oxygen $IrCl(C_2H_4)(O_2)(PPh_3)_2$, in which ethylene can be replaced by other ligands. With sulfur dioxide, $IrCl(C_2H_4)(PPh_3)_2$ and $IrCl(C_3H_4)(PPh_3)_2$ form the adducts $IrCl(C_2H_4)(SO_2)(PPh_3)_2$ and $IrCl(C_3H_4)(SO_2)(PPh_3)_2$.

The stability of five-coordinated compounds of the type $IrCl(PPh_3)_2XY$ is discussed on the basis of the donor and acceptor properties of the ligands X and Y.

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Introduction

Chlorotris(triphenylphosphine)iridium(I), $IrCl(PPh_3)_3$, was recently reported to be inactive in the hydrogenation of alkenes (1) and in the polymerisation of allenes (2). This inactivity might be due to the strong iridium-phosphine bond, which prevents the complex to become unsaturated by dissociation of a phosphine ligand. As was shown in hydrogenation experiments using the corresponding rhodium(I) compound, $RhCl(PPh_3)_3$, such a process enables the metal to activate the substrate (4).

In hydrogenation reactions, we tested the catalytic activity of benzene solutions of the iridium(I)-cyclooctene complex $[IrCl(C_8H_{14})_2]_2$ to which different amounts of triphenylphosphine had been added (3). It was found that the resulting systems were active with respect to the hydrogenation and isomerization of alkenes. The maximum hydrogenation rate at a phosphine/iridium ratio 2 suggested the active species to be chlorobis(triphenylphosphine)iridium(I), $IrCl(PPh_3)_2$*).

We report here the synthesis and properties of $IrCl(PPh_3)_2$ and its addition products obtained by reaction with ethylene, allene, butadiene, oxygen and sulfur dioxide. The method of alkene replacement used to prepare $IrCl(PPh_3)_2$ from $[IrCl(C_8H_{14})_2]_2$ is generally applied in the synthesis of rhodium(I) compounds (4-6).

Experimental section

Materials. Ethylene, butadiene (ex l'Air Liquide), allene, sulfur dioxide (ex Baker Chemicals) were used without purification. All solvents were reagent-grade quality and degassed

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*) The fourth coordination site is probably occupied by a solvent molecule

Table I

Preparation and analysis of chlorobis(triphenylphosphine)iridium(I) complexes

	Compound	Starting from	Procedure
1	$IrCl(PPh_3)_2$	$[IrCl(C_8H_{14})_2]_2$ (0.5 g, 0.56 mmole) in 40 ml benzene + PPh_3 (0.58 g, 2.2 mmole)	Stir mixture for a few minutes, add 80 ml pentane, collect crystals, wash with alcohol, dry under vacuum, store under nitrogen.
2	$IrCl(C_2H_4)(PPh_3)_2(C_6H_6)_{\sim\frac{1}{2}}$	See 1	Stir mixture for a few minutes, bubble through C_2H_4 (15 min), add 80 ml C_2H_4-satd. pentane. Filter off precipitate, wash with pentane, dry under vacuum, store under nitrogen.
3	$[IrCl(C_2H_4)(PPh_3)]_2(C_6H_6)_2$	$[IrCl(C_2H_4)_2]_2$ (0.16 g, 0.29 mmole) in 10 ml benzene + PPh_3 (0.15 g, 0.57 mmole)	Leave 5 min, filter off precipitate, wash with pentane, dry under vacuum, store under argon.
4	$IrCl(C_2H_4)_2(PPh_3)_2$	2 (0.12 g) in 8 ml C_2H_4-satd. chloroform	Cool the solution (orange) to -50°C (colourless), add pentane, decant solvent from precipitate formed, freeze-dry at -50°C for 30 min.
5	$IrCl(C_2H_4)(O_2)(PPh_3)_2(C_6H_6)$	2 (0.30 g) suspended in 20 ml C_2H_4-satd. C_6H_6	Sweep carefully O_2 over slowly stirred soln. until light-red; concentrate by sweeping with C_2H_4, filter off precipitate, dry under vacuum, store under C_2H_4 at -30°C
6	$IrCl(O_2)(PPh_3)_3$	5 (0.15 g) in 15 ml C_2H_4-satd. C_6H_6 + PPh_3 (44.2 mg, 1 eq.)	Stir mixture for 5 min, concentrate solution under argon to 1/3 of orginal volume, add pentane, filter off precipitate, wash with pentane, dry under vacuum, store under nitrogen.
7a	$IrCl(O_2)(PPh_3)_2(C_3H_4)$	5 (0.125 g) suspended in 20 ml C_6H_6 + 1 eq. allene	Stir mixture for 15 min at room temp, add pentane, filter off precipitate, wash with pentane, dry under vacuum
7b	$IrCl(O_2)(PPh_3)_2(CH_3CN)$	5 (0.1 g) suspended in 5 ml CH_3CN	Leave 5 min to obtain soln., add pentane, filter off precipitate, wash with ether, dry under vacuum.
7c	$IrCl(O_2)(PPh_3)_2(AsPh_3)$	See 6; 1 eq. $AsPh_3$	See 6
7d	$IrCl(O_2)(PPh_3)_2(C_5H_5N)$	5 (0.2 g) in 5 ml pyridine	Leave 10 min, add pentane, filter off precipitate, wash with ether, dry under vacuum, store under nitrogen.
8	$IrCl(C_3H_4)(PPh_3)_2$	2 (0.20 g) suspended in 20 ml C_2H_4-satd. C_6H_6	Sweep carefully allene over slowly stirred suspension until yellow solution; concentrate by sweeping with argon, precipitate with pentane.
9	$IrCl(C_3H_4)(SO_2)(PPh_3)$	8 (0.20 g) in 20 ml C_6H_6	Bubble through SO_2 during 30 min, precipitate with pentane
10	$IrCl(C_6H_8)(PPh_3)_2$	2 (0.5 g) suspended in 15 ml alcohol or aceton	Bubble trough allene during 15 min at room temp.; filter off precipitate, wash with toluene, dry under vacuum
11	$IrCl(C_2H_4)(SO_2)(PPh_3)_2C_6H_6$	2 (0.5 g) suspended in 20 ml C_2H_4-satd. C_6H_6	Bubble through SO_2 during 2 min until solution; concentrate by sweeping with C_2H_4, filter off complex, dry under vacuum.
12	$IrCl(C_5H_5N)(SO_2)(PPh_3)_2$	11 (0.15 g) in 4 ml pyridine	Add pentane after 30 min, filter off precipitate, wash with pentane, dry under vacuum.
13	$IrCl(C_4C_6)(PPh_3)_2$	2 (0.30 g) suspended in 20 ml C_2H_4-satd C_6H_6	Bubble through butadiene for 10 min until yellow-red soln., concentrate by sweeping with butadiene, add pentane, filter off precipitate wash with pentane, dry under vacuum.

Yield in % (g)	Elementary analysis calculated / found					Formula for calculated values	Properties
	C	H	Cl	P	other		
78 (0.65)	57.4 57.0	4.0 4.4	4.7 4.5	8.2 8.0		$C_{36}H_{30}ClP_2Ir$	Very O_2 sensitive, pale-yellow crystals
80 (0.70)	60.0 59.4	4.5 4.7	4.3 4.3	7.6 7.6		$C_{41}H_{37}ClP_2Ir$	Yellow-orange M.p. 144°-148°C (dec.)
60 (0.20)	51.1 51.4	4.5 4.5	5.9 5.9	5.3 5.3		$C_{52}H_{50}Cl_2P_2Ir_2$	Pale-yellow υ(Ir-Cl) 250 cm^{-1} $\tau(C_2H_4)$ in $CDCl_3$ at -30°C 6.65 ppm
							White, stable at -50°C
67 (0.21)	59.4 60.3	4.5 4.8	4.0 3.9	7.0 7.2	3.6 2.6 } O	$C_{44}H_{40}ClP_2O_2Ir$	Pale-yellow
70 (0.11)	62.0 61.0	4.3 4.2	3.4 3.3	9.2 9.0		$C_{54}H_{45}ClP_3O_2Ir$	Yellow
79 (0.09)	56.8 54.8	4.1 4.2	4.3 4.6	7.5 7.6		$C_{39}H_{34}ClP_2O_2Ir$	Yellow-brown M.p. 169°-171°C (dec.)
84 (0.07)	55.3 54.1	4.0 3.6	4.3 4.1	7.5 7.3	1.7 2.0 } N	$C_{38}H_{33}ClP_2NO_2Ir$	Light-yellow
70	59.5 58.1	4.1 4.2	3.3 3.7	5.7 6.1	6.9 7.2 } As	$C_{54}H_{45}ClP_2AsO_2Ir$	Yellow
83 (0.16)	57.0 55.4	4.1 4.3	4.1 5.2	7.2 7.0	1.6 1.7 } N 3.7 2.8 } O	$C_{41}H_{35}ClP_2NO_2Ir$	Yellow
65 (0.12)	59.1 58.4	4.3 4.7	4.5 4.5	7.8 7.8		$C_{39}H_{34}ClP_2Ir$	Yellow M.p. 172°-175°C (dec.)
77 (0.17)	54.7 54.9	4.0 4.5	4.2 4.1	7.3 7.0	3.7 3.7 } S	$C_{39}H_{34}ClP_2SO_2Ir$	Yellow-green
85 (0.41)	60.6 61.9	4.6 4.9	4.3 4.3	7.5 7.0		$C_{42}H_{38}ClP_2Ir$	White M.p. > 200°C
72 (0.39)	57.3 57.4	4.3 4.6	3.9 4.1	6.7 6.9	3.5 3.6 } S	$C_{44}H_{40}ClSO_2P_2Ir$	Yellow-green M.p. > 200°C
69 (0.10)	55.1 54.9	3.9 4.1	4.0 4.2	6.9 7.3	3.6 3.6 } S 1.6 1.6 } N	$C_{41}H_{35}ClSO_2NIr$	Yellow
75 (0.22)	60.7 60.7	4.3 4.7	4.3 4.3	7.5 7.3		$C_{40}H_{36}ClP_2Ir$	Pale yellow M.p. 164°-167°C (dec.)

before use. All experiments were carried out under nitrogen or argon. The preparation and the analytical data of the complexes prepared are given in Table I.

Measurements. IR-spectra were measured on Hitachi EPI-G2 (4000-400 cm^{-1}) and Hitachi EPI-L (700-200 cm^{-1}) spectrometers. PMR spectra were recorded on the Varian spectrometers A-60, HA-100 and HR-220 and partly on a Jeol 100. Microanalyses were carried out by Dr A. Bernhardt, Mikroanalytisches Laboratorium, Elbach über Engelskirchen, Germany. Some of the oxygen adducts were analysed by the Analytical Department of the Imperial College of Science and Technology, London, England.

(a) Chlorobis(triphenylphosphine)iridium(I), $[IrCl(PPh_3)_2]_n$

A solution of $[IrCl(C_8H_{14})_2]_2$ in benzene, to which two equivalents of triphenylphosphine are added, catalyses the hydrogenation and isomerization of alkenes (3). From this solution, a fine powder of the light-yellow complex $[IrCl(PPh_3)_2]_n$ (1)*) can be isolated after addition of pentane. Once precipitated, the compound is only slightly soluble in benzene and a solution of the redissolved complex does not show any catalytic activity (7). From this we suppose that the complex is precipitated as an inactive dimer or polymer from the active solution in which it is, at least partly, present as an active monomer. This behaviour would then parallel the properties of the corresponding chloro(triphenylphosphine)rhodium(I) system in which the dimer $[RhCl(PPh_3)_2]_2$ was, in contrast with the monomer, likewise inactive (8). The far IR-spectrum of 1 shows in the ν(Ir-Cl) region a strong absorption at 302 cm^{-1}. It is extremely sensitive to oxygen and in air it forms a grey-green reaction product, which, according to absorption bands at 1120 and 720 cm^{-1} in its IR-spectrum, contains triphenylphosphinoxide.

*) Underlined numbers refer to the compounds in Table I

This reaction product is probable identical to the unidentified product obtained by Collman et al. (9) from the decomposition in air of the molecular nitrogen complex $IrCl(N_2)(PPh_3)_2$. 1 slightly dissolves in chloroform, but by reaction with the solvent it is rather quickly partly oxidized to an iridium(III) complex. This was demonstrated by the reaction of a fresh and an one-hour-old chloroform solution with carbon monoxide. The reaction product of the former was identified on the basis of its IR-spectrum to be Vaska's compound, $IrClCO(PPh_3)_2$, whereas from the latter solution a mixture of compounds was isolated with ν(CO) at 1955 and 2060 cm^{-1}, being indicative of iridium(I) and (III) complexes respectively (10).

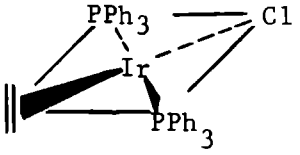
Prepared in situ by the above-mentioned procedure in benzene, 1 undergoes readily addition reactions. Because of its extreme sensitivity towards oxygen and its presumed tendency to form polymers in solution, it sometimes appeared profitable to prepare the ethylene adduct $IrCl(C_2H_4)(PPh_3)_2$ (2) first and to use this complex in situ or after isolation as a starting compound for the preparation of the adducts of 1.

(b) Reaction of $IrCl(PPh_3)_2$ with ethylene

Chlorobis(triphenylphosphine)(ethylene)iridium(I), $IrCl(C_2H_4)(PPh_3)_2$ (2) can be prepared at room temperature by passing ethylene through a benzene solution of $[IrCl(C_8H_{14})_2]_2$ and two equivalents of triphenylphosphine Orange crystals of 2 with about a half solvent molecule of benzene separated after addition of pentane. Alternatively, 2 may be prepared by the addition of two equivalents of triphenylphosphine to a benzene solution of the bis(ethylene) dimer $[IrCl(C_2H_4)_2]_2$ (Ref. 11). In this reaction, one of the ethylene ligands in this dimer is first replaced by a triphenylphosphine ligand, followed by splitting of the chlorine bridge by the second phosphine ligand. This

may be concluded from the immediate precipitation of the dimeric complex $[IrCl(C_2H_4)(PPh_3)]_2$ (4) after addition of one equivalent phosphine.

2 is stable under vacuum, but in air it slowly forms phosphinoxide containing products. It is moderately soluble in $CHCl_3$ and CH_2Cl_2 but reacts slowly with these solvents. The far IR-spectrum shows an iridium-chlorine stretching frequency at 301 cm^{-1} with a weak shoulder at 295 cm^{-1}. Apart from phenyl hydrogen resonances, the weak PMR-spectrum shows a resonance due to coordinated ethylene; in $CDCl_3$ a broad resonance at τ 8.95 and in CD_2Cl_2 an apparent triplet at τ 8.95 ($J_{P-H} \approx 4$ c/s). Unlike solutions of the corresponding rhodium compound (8), the solution of 2 in $CHCl_3$ does not lose ethylene on sweeping with nitrogen, as may be concluded from the unchanged PMR-spectrum. This illustrates the stronger metal-alkene bond in iridium complexes. The spectroscopic data of 2 are in agreement with a square planar structure like the structure (I) of the corresponding tetrafluoroethylene complex $IrCl(C_2F_4)(PPh_3)_2$ with the chlorine ligand trans to the alkene (3,12).



(I) (compound 2)

An orange, ethylene-saturated, chloroform solution of 2 becomes colourless on cooling to -50°C. Addition of pentane precipitates an unstable white compound which cannot be isolated completely free from solvent. At room temperature it decomposes under evolution of ethylene into 2. The ethylene content of the gas sample obtained on pyrolyses at 180°C, as determined by the

Wijs' method, was found to correspond with two molecules of ethylene per iridium atom. We suppose that the white compound is the five-coordinated bis(ethylene) adduct $IrCl(C_2H_4)_2(PPh_3)_2$ (3), which may be considered isostructural with the likewise unstable ethylene adduct of Vaska's compound, $IrCl(CO)(C_2H_4)(PPh_3)_2$ (13).

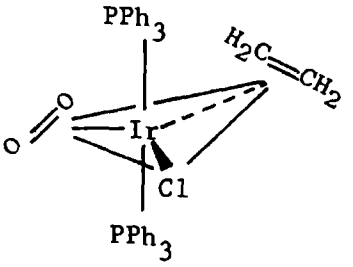
(c) Oxygen adducts of $IrCl(PPh_3)_2$

A suspension of 2 in benzene reacts with molecular oxygen, forming triphenylphosphinoxide containing products. In the presence of one equivalent of free ethylene, however, the diamagnetic oxygen complex $IrCl(C_2H_4)(O_2)(PPh_3)_2(C_6H_6)$ (5) is rapidly formed. This suggests that this reaction proceeds via the unstable bis(ethylene) adduct 3. A possible explanation may be that 3 produces upon dissociation of one ethylene ligand a reactive non-planar four-coordinated intermediate, which is then supposed to react fast with an oxygen molecule before it adopts the less reactive square planar form. Alternatively, 3 may undergo an associative substitution process in which a six-coordinated intermediate is involved. Such a process has been shown to occur in the penta-coordinated $IrCl(C_2H_4)_4$ during ethylene exchange (11).

The oxygen addition is irreversible and the compound does neither loose oxygen nor ethylene under vacuum (5 h). It has a very low solubility in most solvents, but it is moderately soluble in chlorinated solvents in which it decomposes slowly.

The weak PMR-spectrum at $-50^{\circ}C$ of the benzene-solvated product in $CDCl_3$ shows resonances at τ 2.73 and 6.65 due to aromatic protons and ethylene protons respectively. The IR-spectrum is characterized by a sharp absorption band at 880 cm^{-1} indicative of a structure in which the two oxygen atoms coordinate to the metal forming an isosceles triangle: the $\overline{O\text{-}Ir\text{-}O}$ ring (14). The iridium-chlorine stretching frequency is at

307 cm^{-1}. This value compares with the ν(Ir-Cl) frequency at 315 cm^{-1} in the oxygen adduct of Vaska's compound $IrCl(CO)(O_2)(PPh_3)_2$, which has been shown by X-ray investigation (15) to possess a trigonal bipyramidal structure II. So we tentatively suggest a similar structure for this compound.



(II) (compound 5)

The ethylene ligand in 5 can be substituted by other ligands under formation of complexes of the type $IrCl(O_2)(PPh_3)L$ with L = triphenylphosphine (6), allene (7a), acetonitrile (7b), triphenylarsine (7c) and pyridine (7d). The complexes 6 and 7a can also be prepared directly from $IrCl(PPh_3)_3$ and $IrCl(C_3H_4)(PPh_3)_2$ (8) respectively by reaction with molecular oxygen.

Table II

"ν(O-O)" in $IrCl(O_2)(PPh_3)_2L$ (in KBr)

Complex	L	ν(O-O) in cm^{-1}
7a	C_3H_4	890[a]
5	C_2H_4	880
7b	CH_3CN	862
Ref. 10	CO	857
7c	$AsPh_3$	854
6	PPh_3	848
7d	C_5H_5N	844

a) 840 cm^{-1} in $^{18}O_2$-adduct

Like the parent compound, the complexes 6 and 7a-d are characterized by strong IR-absorption bands between 800 and 900 cm^{-1} (Table II). The allene compound 7a exhibits two absorptions in the 800-900 cm^{-1} region, e.g. at 890 and 862 cm^{-1}. Isotopic substitution with $^{18}O_2$ shifts the former band to 840 cm^{-1}, leaving the position of the other band unchanged. The magnitude of the shift equals the mass effect calculated for a simple harmonic oscillator. The 862 cm^{-1} band is assigned to the $\delta(CH_2)$ vibration of the allene ligand. This assignment is also supported by the presence of a weak overtone of this fundamental at 1724 cm^{-1} (see Table III).

As is shown in Table II, the position of the characteristic absorption depends on L. In view of the insensitivity of this frequency to the O-O bond length, it was earlier suggested that this mode was not a pure O-O stretching vibration and that it might mix with the symmetrical metal-oxygen vibration (14).

Table III

IR- and PMR-spectra of allene complexes
($\delta(CH_2)$ data refer to the fundamental and the overtone frequency)

Compound $MCl(C_3H_4)(PPh_3)_2L$			IR-data in cm^{-1}		τ-values in $CDCl_3$ (ppm)	
Complex No.	M	L	ν(C=C)	$\delta(CH)_2$	uncoordinated CH_2	coordinated CH_2
8	Ir	-	1719	816, 1634	5.65(1), 5.92(1)	9.47(2)
Refs. 16,17	Rh	-	1730	835	5.65(1), 5.92(1)	9.47(2)
7a	Ir	O_2	1760	862, 1724	3.97(1), 5.32(1)	7.34(2)
-	Ir	CO	1708	831, 1662		
9	Ir	SO_2			4.36(1), 5.33(1)	8.77(2)[a]

[a] Apparent triplet, $J_{P-H} \approx 3$ c/s

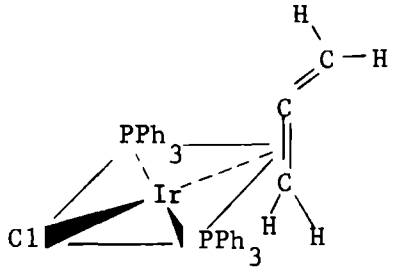
(d) Reactions of $IrCl(PPh_3)_2$ with allene

A solution of 1 or a suspension of 2 in benzene immediately reacts with one equivalent of allene forming the yellow complex $IrCl(C_3H_4)(PPh_3)_2$ (8). On exposure to air, 8 forms the oxygen adduct 7a. As mentioned under (c), this complex can also be obtained by treatment of a benzene suspension of the oxygen-ethylene adduct 5 with one equivalent of allene. The reaction product of 8 with sulfur dioxide is $IrCl(C_3H_4)(SO_2)(PPh_3)_2$ (9). Treatment of Vaska's compound, $IrCl(CO)(PPh_3)_2$, with allene in benzene yields the unstable $IrCl(CO)(C_3H_4)(PPh_3)_2$. This compound loses allene on exposure to air within 10 minutes, but is stable in an allene atmosphere.

The IR-spectra (Table III) of these mono-allene complexes are, with the exception of 9 (see next section), characterized by a ν(C=C) absorption band of medium intensity in the 1700 cm^{-1} region and a strong $\delta(CH_2)$ band in the 800-900 cm^{-1} region with its weak overtone band at twice the fundamental frequency. These absorption bands are also found (17) in the spectrum of the rhodium complexes $RhX(C_3H_4)(PPh_3)_2$ (X=Cl, Br or I) and are indicative of the presence of allene coordination using only one double bond. The far IR-spectrum of 8 reveals a band at 309 cm^{-1} with a shoulder at 303 cm^{-1}, which we assign to the ν(Ir-Cl) mode. The instability of 8 in chloroform and its low solubility in other solvents prevents PMR investigations. The structure of 8 is thought to be similar to the structure of $RhI(C_3H_4)(PPh_3)_2$, which can be described as square planar with the phosphine ligands in trans-position and the bended C=C=C system of the allene ligand approximately perpendicular to the molecular plane and coordinated to the metal through one C=C bond, the other C=C bond being bended away from the metal (18) (Structure III).

Treatment of $IrCl(PPh_3)_3$ or complex 8 with excess of allene resulted in the formation of the white coloured complex

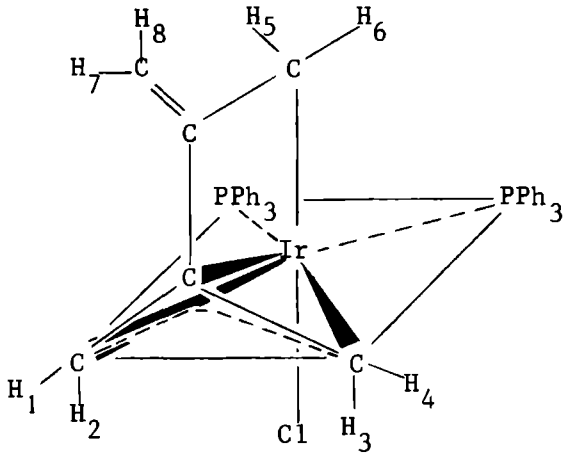
$IrCl(C_6H_8)(PPh_3)_2$ (10), which showed characteristic IR-absorption bands at 2881, 1654, 944, 916 and 878 cm^{-1}.



(III) (compound 8)

X-ray investigation (19) showed that the iridium atom was six-coordinated with two cis-phosphine ligands and a tridentate 2,2'-bi-σ,π-allyl ligand formed by allene dimerization (Structure IV). The position of Cl trans to the σ-bonded CH_2-group accounts for the low position of ν(Ir-Cl) at 253 cm^{-1}.

The PMR resonances of the CH_2-groups trans to the phosphine ligands at τ 9.37 (2, broad) and τ 7.33 (2, doublet J_{P-H} = 8 c/s) indicated coupling with P^{31}-nuclei.



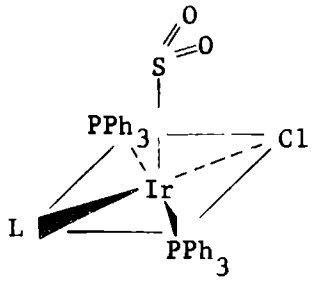
(IV)(compound 10)

On account of the τ- and the J_{P-H}-value, we assign the former resonance to $H_{2,3}$ and the latter to $H_{1,4}$. The resonance of the protons $H_{5,6}$ was a sharp singlet at τ 6.85, whereas the uncoordinated protons $H_{7,8}$ located in the plane of symmetry of the molecule gave rise to two singlets at τ 5.71 and 5.86.

Unlike its rhodium analogue, $IrCl(PPh_3)_3$ is not a good catalyst for the oligomerization of allene (2). This is certainly due to the strong iridium-phosphorus bond which prevents further phosphine dissociation in complex 10 by which this complex can become coordinately unsaturated and activate another allene molecule*).

(e) Sulfur dioxide adducts

Treatment of 2 and 8 with SO_2 in benzene resulted in the formation of the adducts $IrCl(C_2H_4)(SO_2)(PPh_3)_2$ (11) and $IrCl(C_3H_4)(SO_2)(PPh_3)_2$ (9) respectively (Structure V). Both compounds are stable under vacuum and in air. They are only slightly soluble in benzene and chloroform.



(V) (compound 9,11)

*) This view is supported by the catalytic activity at 70°C in alcohol-dichloromethane of the corresponding complex $IrCl(C_6H_8)(AsPh_3)_2$ containing the weaker iridium-arsine bonds. The IR-spectrum of the resulting poly-allene (m.p. 114-117°C) shows absorption bands due to unconjugated vinylidene groups.

The PMR spectrum in $CDCl_3$ of 11 shows resonances at τ 2.73 and 7.68 due to aromatic and ethylene protons respectively. Although the IR-spectrum of 9 did not show the characteristic ν(C=C) absorption in the 1600-1800 cm^{-1} region, its PMR spectrum proved the presence of allene (Table III).

The coordination geometry around the metal in 9 and 11 is probably similar to that in $MCl(CO)(SO_2)(PPh_3)_2$ with M = Rh(20) or Ir (21), which is described as tetragonal pyramidal with CO, Cl and the trans P-atoms in the base and the S of the SO_2 group at the apex.

The IR-spectra (Table IV) show strong absorption bands indicative of a SO_2-ligand, sulfur-bonded to the metal and acting as a σ-Lewis acid (20,22). With this type of bonding, the metal-SO_2 moiety has a pyramidal structure with the S at the apex. This structure contrasts with the planar structure of the metal-SO_2 moiety found (23) in the complex $[RuCl(NH_3)_4SO_2]Cl$. Here the SO_2-ligand is acting as a Lewis base, and the metal-sulfur bond is shortened by multiple π-bonding.

Table IV

IR-spectra of SO_2-complexes

Compound $MCl(SO_2)(PPh_3)_2L$			SO_2-absorption bands (cm^{-1})	
Complex No.	M	L	ν_{sym}	ν_{asym}
11	Ir	C_2H_4	1063	1215, 1190
9	Ir	C_3H_4	1040	1215, 1190
Ref. 22	Ir	CO	1048	1198, 1185
Ref. 22	Rh	CO	1057	1214, 1188
Ref. 23	$[RuCl(NH_3)_4(SO_2)]Cl$		1100	1301, 1278

(f) Butadiene adduct of $IrCl(PPh_3)_2$

Treatment of a benzene suspension of 2 with butadiene for about ten minutes followed by addition of pentane gave the pale-yellow compound $IrCl(C_4H_6)(PPh_3)_2$ (13). The same complex can also be isolated by treatment of $IrCl(C_4H_6)_2$ (Ref. 11b) with two equivalents of triphenylphosphine. The PMR-spectrum at 60 and 100 MHz in $CDCl_3$ show broadened resonances at τ 4.44(1), 4.96(1), 6.92(1), 9.10(1), 10.18(1) and 10.78(1). The iridium-chlorine stretching frequency is at 276 cm^{-1} with a shoulder at 282 cm^{-1}. For rhodium the four-coordinated species $RhCl(C_4H_6)(PPh_3)$ has been reported (24)*).

Five-coordination

The tendency of transition metals to form penta-coordinated complexes depends on the metal, its oxidation state and on the ligands surrounding it. Shriver (25) discussed the stability of low-oxidation-state metal complexes with Lewis acid ligands, such as BF_3, BH_3, O_2, SO_2 and tetracyanoethylene, on the basis of the transition-metal basicity concept. So the increased stability of five-coordinated complexes going from rhodium(I) to iridium(I) parallels the increased basicity going down from the second to the third row in the transition metal group.

The influence of the nature of the X and Y ligands on the stability of the five-coordinated complexes of the type $IrCl(PPh_3)_2XY$ is very pronounced. In Table V the occurrence and stability of these complexes are summarized; the ligands are divided into three groups:

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*) Misprints in this reference may lead to the erroneous conclusion that the five-coordinated complex $RhCl(C_4H_6)(PPh_3)_2$ was reported.

(I) ligands posessing primarily accepting properties (sulfur dioxide, oxygen, tetrafluoroethylene);

(II) "biphilic" ligands with donor and acceptor abilities (ethylene, allene, carbon monoxide);

(III) primarily donating ligands (pyridine and triphenylphosphine).

Table V

Occurrence and stability of pentacoordinated complexes of the type $IrCl(PPh_3)XY$

(?) Occurrence unknown, (+) isolated under normal conditions, (-) unstable under normal conditions

Y \ X		I			II			III	
		C_2F_4	O_2	SO_2	CO	C_3H_4	C_2H_4	PPh_3	C_5H_5N
I	C_2F_4	?							
	O_2	?	?						
	SO_2	?	?	?					
II	CO	+[a]	+[a]	+[a]	-[a]				
	C_3H_4	?	+(7a)	+(9)	-	b			
	C_2H_4	?	+(5)	+(11)	-[a]	?	-(4)		
III	PPh_3	+[c]	+(6)	?	?	?	?	?	
	C_5H_5N	?	+(7d)	+(12)	?	?	?	?	?

a) Ref. 10

b) Occurrence concluded from formation of $IrCl(C_6H_8)(PPh_3)_2$ (10)

c) Ref. 12

Molecular orbital calculations on Pt(II)-complexes with σ-donating ligands showed that the original metal-ligand bonds all weaken upon expansion of the coordination number from four to five (26). This opposes the gain of the bond energy of the fifth metal to ligand bond. The same is likely to be true for complexes with primarily π-accepting ligands because of the competition for the metal-electron density. From this point of view, the

absence of known complexes of the type $IrCl(PPh_3)_2XY$ with X and Y belonging both to group I or both to group III may be understood*).

Our results indicate that five-coordination is especially favoured by the presence of X and Y ligands which are strongly complementary in their donor and acceptor properties. The nature of metal may be described as "dualistic" in the sense that it acts as a base towards ligands with acid properties and vice versa. Noteworthy is the non-existence of complexes in which the amphoteric group II ligands combine with the donating group III ligands, whereas with the acidic group I ligands stable complexes are formed. This seems to confirm Vaska's suggestion (28) that σ-basicity of these amphoteric ligands appears to be an even more important feature than their acid function in these complexes. The instability of the complexes with X and Y being both amphoteric may be considered as the result of this weak σ-basicity of these ligands and the weakening of the other metal ← ligand σ-bonds on expandion of the coordination number from four to five.

Acknowledgement

We thank Professors A. van der Avoird and D.A. van Dorp for their stimulating interest and Mr H. van Gaal for fruitful discussions. We are grateful to Dr M. van Gorkom, Messrs J. Barzilay and R.W. Schaier for measurement of the NMR-spectra.

*) It is known from thermochemical studies (27) that the entropy of formation of five-coordinated adducts of $IrCl(PPh_3)_2(CO)$ amounts -20 to -40 eu, corresponding with a free-energy contribution of about 10 kcal/mole at room temperature. So, in order to be stable at room temperature, the enthalpy of formation of five-coordinated complexes has to be larger than about -10 kcal/mole.

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SUMMARY

In this thesis the synthesis and properties of several iridium(I) complexes are described. The synthetic routes are mainly based on ligand substitution and addition on the versatile starting compounds chloro- and bromobis(cyclooctene)iridium(I). For the chloro compound a detailed description of a convenient synthesis with about 80% yield is given. The synthetic routes are summarized in Schemes 1 and 2 on pp 83 and 84.

Several compounds are connected in one or other way with the catalysis of alkene reactions. Benzene solutions of $[IrCl(C_8H_{14})_2]_2$ with 0-2 equivalents of triphenylphosphine isomerize and hydrogenate hexene-1(Ref.1). $IrCl(C_6H_8)(PPh_3)_2$ may be regarded as a model for a reaction intermediate in allene polymerization reactions in which the allene dimer is captured as the 2,2'-bi-σ,π-allyl ligand.

A comparison of the far-IR spectra of the chloro- and bromo(alkene)iridium(I) compounds enabled us to assign the iridium-chloro stretching vibrations. These vibrations were found at higher frequencies than the metal-chloro stretching vibrations in the corresponding rhodium(I) compounds. The same mutual position was found for the bands ascribed to the metal-ethylene stretching modes in the chlorobis(ethylene) compounds. These results show that iridium(I) complexes are characterized by stronger metal-chlorine as well as stronger metal-alkene bonds than the corresponding rhodium(I) complexes. This is in agreement with reported better overlap between iridium and ligand orbitals and is illustrated by the recently found iridium-chlorine bond length of 2.416(3)Å in $IrCl(C_4H_6)_2$ (Ref. 2) which is significantly shorter than the rhodium-chlorine distance (2.450(5)Å) in the isomorphous $RhCl(C_4H_6)_2$ (Ref. 3).

The proton spin-lattice relaxation behaviour of solid $IrCl(C_2H_4)_4$ was measured and explained on the basis of alkene

rotation around the metal-alkene axis. The activation energy of the reorientations is 1.6 kcal/mol for the axial and 5.3 kcal/mol for the equatorial ethylene ligands. Our failure to freeze out the ethylene resonances in the PMR-spectrum of $Ir(acac)(C_2H_4)(C_2F_4)$ suggests a likewise low value for the barrier to ethylene rotation in this compound.

The literature reports values between 10 and 15 kcal/mol for alkene reorientation in platinum(II) and rhodium(I) complexes. The low barrier to ethylene reorientation we found may be due to the presence of ligands with sufficient π-backbonding capacity viz. the other three ethylene ligands in $IrCl(C_2H_4)_4$ and the tetrafluoroethylene ligand in $Ir(acac)(C_2H_4)(C_2F_4)$. These ligands compete with the rotating ethylene ligand for the metal electron density and may also act as electron sinks to and from which the electron density shifts during the rotation flip of the ethylene ligand.

Ethylene exchange of the related complexes $Ir(acac)(C_2H_4)_2$ and $Ir(acac)(C_2H_4)(C_2F_4)$ with free ethylene was investigated qualitatively by high resolation PMR. The process appeared to have a mainly associative character but was fast in the former and slow in the latter case. From these experiments and the different behaviour of both compounds towards Lewis bases it was concluded that ethylene acts as a Lewis acid towards the metal during the alkene activation. Coordinated C_2F_4 is generally considered as a strong π-acid. However, its weak acidic character during its activation was concluded from its low reactivity towards metal complexes. The difference in character of free and coordinated C_2F_4 was rationalized by considering the repelling interactions between the non-bonded p-electrons on the fluorine substituents with the alkene π-system in the flat and uncoordinated C_2F_4 molecule and the σ-inductive influence of the fluorine atoms in the bended coordinated C_2F_4 ligand.

The ethylene exchange of $IrCl(C_2H_4)_4$ with free ethylene seemed to be an associative process. Since the metal has 18 electrons in its valence shell the incoming ethylene molecule is also on this occasion expected to act as a Lewis acid towards the metal. Other examples of reactions in which complexes of transition metals with 18 valence electrons react with Lewis acids are known from the literature (Ref. 4).

The tendency of transition metals to form five-coordinated complexes depends on the metal, its oxidation state and on the ligands surrounding it. The increased stability of five-coordinated complexes going from rhodium(I) to iridium(I) parallels the increased overlap between metal and ligand going down from the second to the third row in the transition metal group. We found that C_2F_4-coordination enhances the ability of iridium(I) to a greater extent than the ability of rhodium(I) to form five-coordinated complexes with donating ligands. This enhancement on C_2F_4 coordination illustrates the dualistic nature of both metals by which they act as a base towards accepting or acidic ligands and as an acid towards donating or basic ligands. In agreement with this dualistic character of the metal we found that the stability of five-coordinated complexes of the type $IrCl(PPh_3)_2XY$ was especially favoured if the X and Y ligands (e.g. O_2, SO_2, pyridine) were strongly complementary in their donor and acceptor properties.

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SAMENVATTING

In dit proefschrift worden de bereiding en de eigenschappen van verschillende iridium(I) verbindingen beschreven. De bereidingen zijn hoofdzakelijk gebaseerd op ligand-substitutie in en ligand-additie aan de uitgangsverbindingen chloro- en bromobis(cycloocteen)iridium(I). Voor de bereiding van de chloorverbinding met een opbrengst van 80% wordt een gedetailleerd voorschrift gegeven. De synthese reacties zijn in de schema's 1 en 2 op pag. 83 en 84 samengevat.

Verscheidene van de beschreven verbindingen zijn op een of andere manier betrokken bij de katalyse van alkeenreacties. Oplossingen van $[IrCl(C_8H_{14})_2]_2$ in benzeen met 0-2 equivalenten triphenylphosphine isomeriseren en hydrogeneren hexeen-1 (Ref. 1). $IrCl(C_6H_8)(PPh_3)_2$ kan beschouwd worden als een model voor een intermediair in polymerisatiereacties van alleen, waarin het alleen dimeer gebonden is als het 2,2'-bi-σ,π-allyl ligand.

Een vergelijking van de ver-infrarood spectra van de chloro- en bromo(alkeen)iridium(I)verbindingen stelde ons in staat de iridium-chloor rekvibraties toe te kennen. Deze vibraties werden bij hogere frekwenties gevonden dan de metaal-chloor rekvibraties in de overeenkomstige rhodium(I)verbindingen. Dezelfde onderlinge posities werden ook gevonden voor de metaal-alkeen rekvibraties. Deze resultaten tonen aan dat iridium(I)verbindingen in vergelijking met de overeenkomstige rhodium(I)verbindingen zowel door sterkere metaal-chloor als door sterkere metaal-alkeen bindingen gekenmerkt worden. Dit komt overeen met de uit de literatuur bekende waarden van de overlapping tussen metaal- en ligandorbitals en wordt bovendien geïllustreerd door de onlangs gevonden iridium-chloor bindingslengte van 2,416(3)Å in $IrCl(C_4H_6)_2$ (Ref. 2) die korter is dan de rhodium-chloor afstand van 2,450(5)Å in het isomorphe $RhCl(C_4H_6)_2$ (Ref. 3).

Het gedrag van de protonspin-rooster relaxatie in vast $IrCl(C_2H_4)_4$ werd gemeten en uit de rotaties van de ethyleenliganden rond de metaal-alkeen bindingsas verklaard. De activeringsenergie

van de heroriëntatie is 7,6 kcal/mol voor de axiale en 5,3 kcal/mol voor de equatoriale ethyleenliganden. De onmogelijkheid de ethyleenresonantie in het PMR spectrum van $Ir(acac)(C_2H_4)(C_2F_4)$ "uit te vriezen" doet een soortgelijk lage rotatiebarrière in deze verbinding vermoeden.

In de literatuur worden waarden van 10 tot 15 kcal/mol genoemd voor de heroriëntatie van alkenen in platina(II)- en rhodium(I)verbindingen. De door ons gevonden lage waarden voor de rotatiebarrières kunnen toe te schrijven zijn aan de aanwezigheid van liganden met voldoende capaciteit voor π-backbonding, te weten de drie andere ethyleenliganden in $IrCl(C_2H_4)_4$ en het C_2F_4-ligand in $Ir(acac)(C_2H_4)(C_2F_4)$. Deze liganden dingen met het roterende ethyleenligand mee naar de electronendichtheid op het metaal en kunnen ook dienst doen als electronenbuffers, waarvan de electronenbezetting tijdens de rotatie vergroot of verkleint.

Met "high-resolution PMR" werd de uitwisseling van ethyleen in de verwante complexen $Ir(acac)(C_2H_4)_2$ en $Ir(acac)(C_2H_4)(C_2F_4)$ met vrij ethyleen kwalitatief onderzocht. Het proces bleek voornamelijk associatief maar was snel in de eerste en langzaam in de laatste verbinding. Uit deze experimenten en het verschillend gedrag van beide verbindingen tegenover Lewis basen werd geconcludeerd dat ethyleen tijdens de activering zich t.o.v. het metaal als een Lewis zuur gedraagt. Hoewel gecoördineerd C_2F_4 gewoonlijk beschouwd wordt als een sterk π-zuur, duidt de lage reactiviteit met metaalverbindingen evenwel op een zwak zuur karakter tijdens de activering. Het verschillend karakter van vrij en gecoördineerd C_2F_4 werd verklaard door in het vlakke en ongecoördineerde C_2F_4-molekuul de afstotende interactie tussen de non-bonded p-electronen van de fluoratomen en het π-systeem en in het gebogen en gecoördineerde C_2F_4-ligand het σ-inductief effect van de fluoratomen in beschouwing te nemen.

De uitwisseling van gebonden ethyleen in $IrCl(C_2H_4)_4$ met vrij ethyleen schijnt eveneens een associatief proces te zijn. Aangezien het metaal hier 18 electronen in de valentieschil herbergt

moet men aannemen dat het inkomende ethyleenmolekuul zich ook hier als een Lewis zuur gedraagt. Andere voorbeelden van reacties waarin complexen van metalen met 18 electronen in de valentieschil reageren met Lewis zuren zijn bekend uit de literatuur (Ref. 4).

Het vermogen van overgangsmetalen om vijf-gecoördineerde verbindingen te vormen hangt af van de aard en de oxidatietoestand van het metaal en van de aan het metaal gebonden liganden. De verhoogde stabiliteit van vijf-gecoördineerde iridium(I)complexen t.o.v. overeenkomstige rhodium(I)complexen gaat samen met de grotere waarden van de overlapping tussen metaal- en ligandorbitals. Wij vonden dat de coördinatie van C_2F_4 wat betreft het vermogen om vijf-gecoördineerde verbindingen met donerende liganden te vormen op iridium(I) een grotere invloed had dan op rhodium(I). De invloed van C_2F_4-coördinatie illustreert het dualistisch karakter van beide metalen waardoor zij zich als een base tegenover accepterende of zure liganden en als een zuur tegenover donerende of basische liganden gedragen. In overeenstemming met dit dualistisch karakter vonden we dat de stabiliteit van vijf-gecoördineerde complexen van het type $IrCl(PPh_3)_2XY$ in het bijzonder begunstigd werd als de X en Y liganden (b.v. O_2, SO_2, pyridine) sterk complementair waren in hun donerende en accepterende eigenschappen.

Referenties

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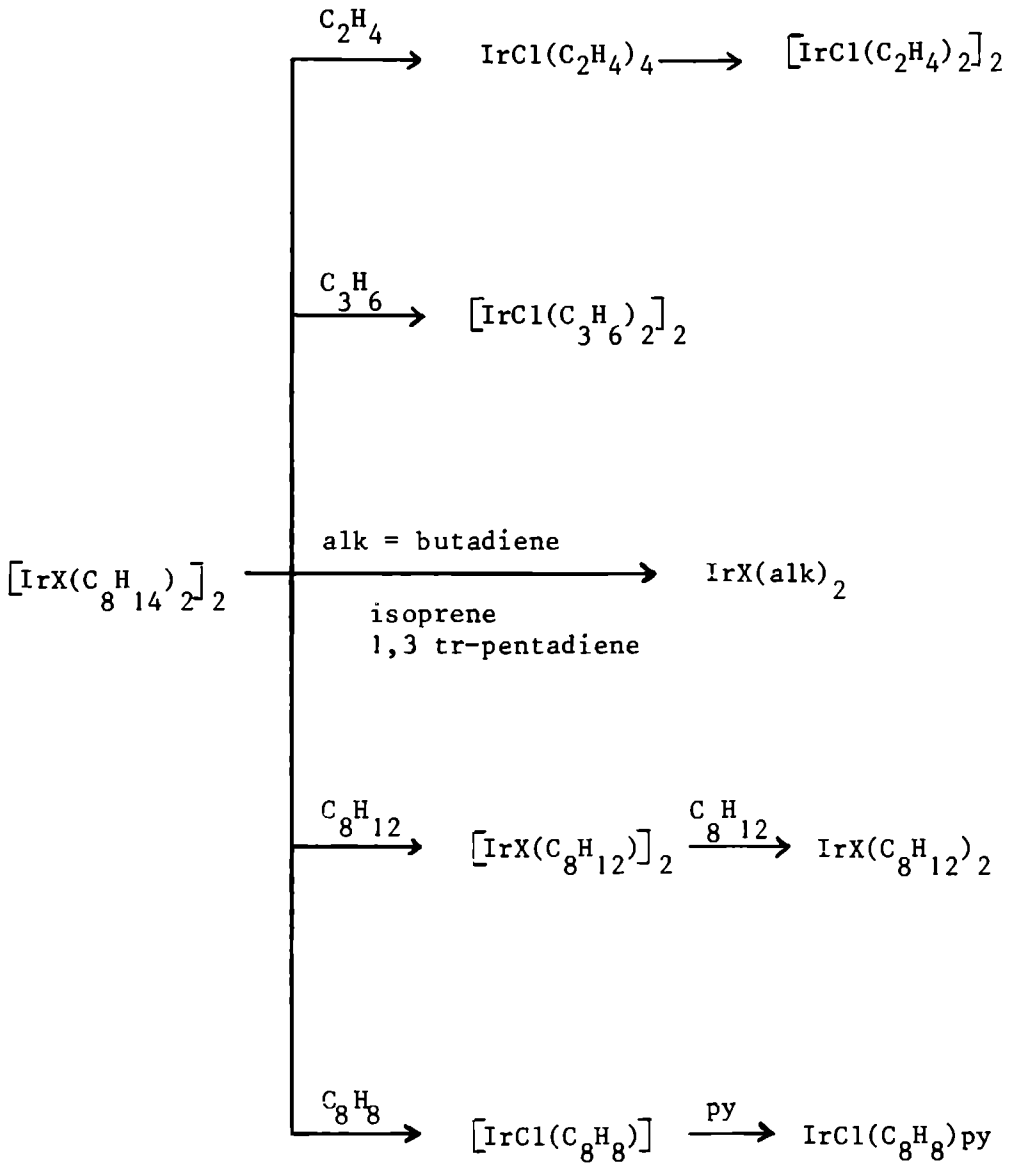
4. C.A. Tolman, Chem. Soc. Rev. 337 (1972).

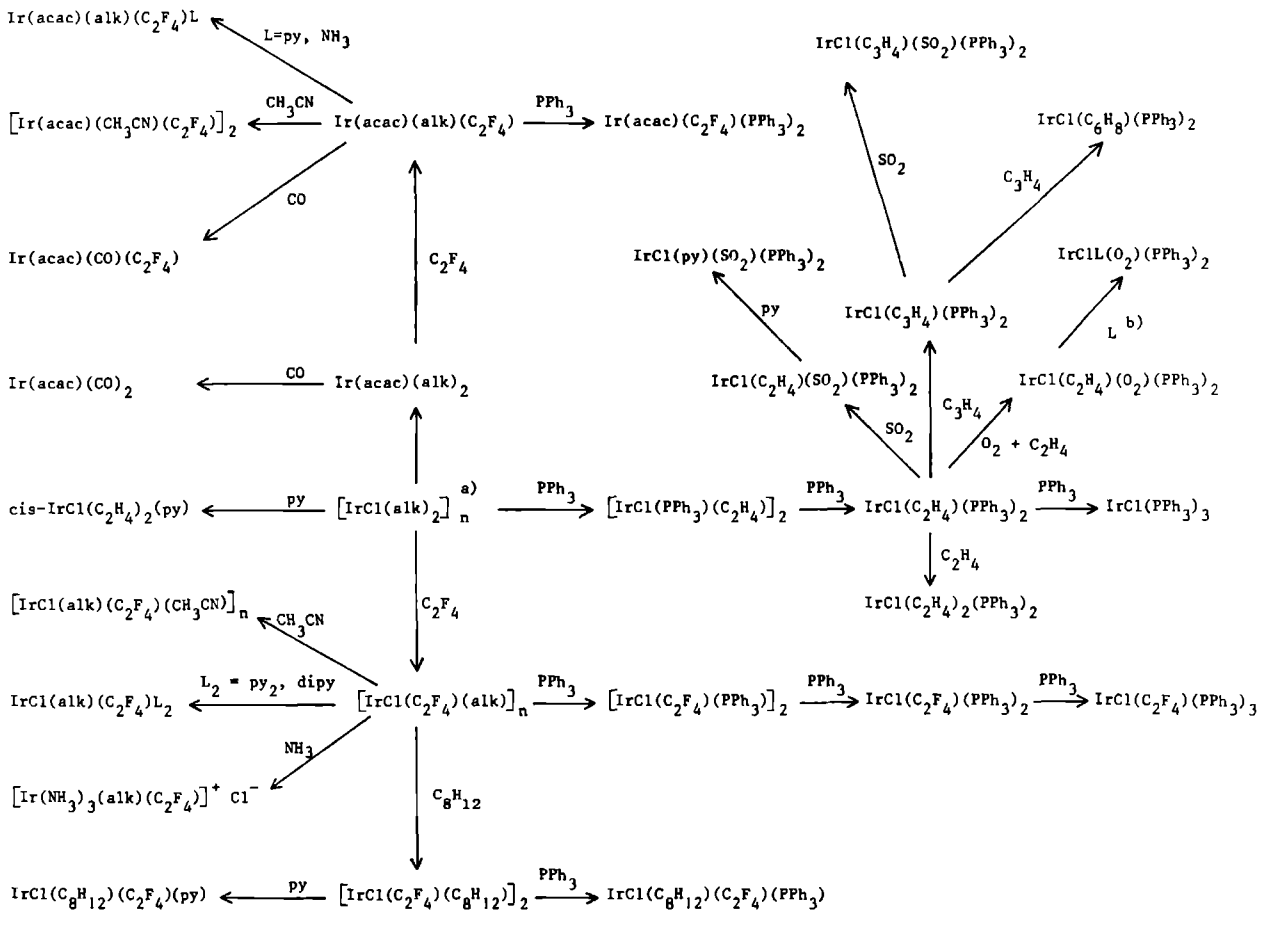
SCHEME 1

Alkene substitution in $[IrX(C_8H_{14})_2]_2$ with X = Cl or Br



SCHEME 2

Synthetic routes to iridium(I) compounds



a) alk = C_2H_4, C_8H_{14}

b) L = PPh_3, $AsPh_3$, C_3H_4, CH_3CN, pyridine

LEVENSLOOP van

Adrianus van der Ent, geboren 23 juni 1936 te Rotterdam.

In 1956 behaalde ik het diploma Chemische Techniek aan de HTS te Dordrecht. Na het vervullen van de militaire dienstplicht trad ik in december 1958 als research-assistent in dienst van het Unilever Research Laboratorium te Vlaardingen.

In 1960 begon ik op parttime basis mijn studie in de chemie aan de Rijksuniversiteit te Leiden, waar mij in november 1962 het kandidaatsexamen werd afgenomen. In januari 1966 werd aan de Rijksuniversiteit te Utrecht het doctoraal examen cum laude afgelegd met als hoofdvak theoretische chemie en als bijvak natuurkunde.

Sinds begin 1966 ben ik op het Unilever Research Laboratorium te Vlaardingen betrokken bij het onderzoek van de eigenschappen en werking van homogene katalysatoren. Eind 1966 en begin 1967 ben ik enige maanden onder leiding van professor G. Wilkinson werkzaam geweest op het Imperial College of Science and Technology te London.

STELLINGEN

1. Volgens Strohmeier en Endres bezitten rhodiumverbindingen een grotere activiteit als katalysator in hydrogeneringsreacties dan de corresponderende iridiumverbindingen. Dit is in zijn algemeenheid onjuist.

   W. Strohmeier en R. Endres, Z. Naturforschung B27, 1415(1972)

2. De intensiteit van de C-C rekvibraties van symmetrische alkenen en alkynen die aan overgangsmetalen zijn gecoördineerd wordt grotendeels bepaald door electronenverschuivingen in de metaal-ligand binding tijdens de vibratie. Het is aannemelijk dat de bijdrage van de π-component van deze binding een relatief grotere bijdrage levert aan de verschuiving dan de σ-component.

3. Tomaselli en Shamos constateren dat de 'critische hydratatie' bij wateradsorptie op collageen afhankelijk is van de frequentie. Dit kan verklaard worden uit de verschillende bindingssterkten tussen de geadsorbeerde watermoleculen en het collageenoppervlak.

   V P. Tomaselli en M.H. Shamos, Biopolymers 12, 353(1973)

4. De interpretatie door Burlingame en medewerkers van ^{13}C-spectra van methylpalmitoleaat is onjuist. De door hen geregistreerde spectra kunnen ook bij juiste interpretatie niet dienen als basis voor hun conclusie dat het via biosynthese verkregen monster alternerend gemerkt is.

   A.L. Burlingame, B. Balogh, J. Welch, S. Lewis en D. Wilson, Chem. Comm 318(1972)

5. Uit het door W J. O'Brien beschreven mathematisch model voor de oppervlaktespanning van vloeistoffen in gesloten capillairen volgt niet noodzakelijkerwijs een afwijkend gedrag van de oppervlaktespanning.

   W.J O'Brien, Surface Science 19, 387(1970)

6. Witzel en Becker gaan uit van een onjuiste probleemstelling bij hun poging de eenheidscel van de stabiele β-modificatie van cacaoboter te bepalen. Bovendien is de poederdiffractie-methode die zij voor het vermeende probleem gebruiken, ontoereikend.

   H. Witzel en K. Becker, Fette Seifen Anstrichmittel 71, 507 (1969)

7. In het door de American Oil Chemists' Society gepubliceerde rapport over de bepaling van het percentage vaste fase in vetten met behulp van wide-line NMR dienen de vulhoogte en de plaatsing van de monsterbuis ten opzichte van de meetspoel te worden vastgelegd.

   J. Amer. Oil Chem. Soc. 49, 431A(1972)

8. Bij pogingen de conformatie van δ-lactonen met behulp van de IR carbonylrekfrekwentie te bepalen moet rekening worden gehouden met evenwichten tussen "boat" en "half-chair" conformaties.

   K.K. Cheung, K.H. Overton en G.A. Sim, Chem. Comm. 634(1965)
   O. Korver, Tetrahedron, 26, 2391(1970)

9. De huidige wet op de ondernemingsraden geeft bij het spel om de knikkers ruime gelegenheid tot schoffelen.

Proefschrift van A. van der Ent
Nijmegen, oktober 1973